THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

APRIL 1927.

LXXXIV. *Electrostatic Problems concerning certain Inverted Spheroids.* *By* D. M. WRINCH, *M.A., D.Sc., Lecturer at Lady Margaret Hall and St. Hilda's College, Oxford* *.

Introduction.

1. IN this paper we consider an analytical treatment of various problems of electrostatics associated with the surfaces obtained by inverting an oblate spheroid with respect to a point on the axis of symmetry.

We may take coordinates (ξ, η, ω) defined by the relations:

$$z' = a'(\cos\eta \sinh\xi + \sinh\xi_1),$$

$$x' = a' \sin\eta \cosh\xi \cos\omega,$$

$$y' = a' \sin\eta \cosh\xi \sin\omega.$$

Then the surfaces $\xi =$ constant are the confocal oblate spheroids:

$$(z' - a' \sinh\xi_1)^2/a'^2 \sinh^2\xi + (x'^2 + y'^2)/a'^2 \cosh^2\xi = 1,$$

and the surfaces $\eta =$ constant are the confocal hyperboloids of revolution of one sheet:

$$(z' - a' \sinh\xi_1)^2/a'^2 \cos^2\eta - (x'^2 + y'^2)/a'^2 \sin^2\eta = 1.$$

The centre of coordinates $(x'\ y'\ z')$ is then at a distance $(-a' \sinh\xi_1)$ from the centre of the spheroids in the direction of the minor axes. The particular spheroid $\xi = \xi_0$ will

* Communicated by the Author.

have the centre of coordinates inside or outside or on it according as

$$\xi_0 = \xi_1, \quad \xi_0 > \xi_1, \quad \xi_0 = \xi_1.$$

It is convenient to use also the variables :

$$\mu = \cos\eta, \quad \nu = \sinh\xi,$$

in terms of which

$$z' = a'(\mu\nu + \nu_1),$$
$$\rho' = (x'^2 + y'^2)^{1/2} = a'[(1-\mu^2)(\nu^2+1)]^{1/2}$$

and we shall also use r' for the distance from the centre of coordinates, given by

$$r' = (z'^2+\rho'^2)^{1/2} = a'(\nu^2 - \mu^2 + 1 + 2\mu\nu\nu_1 + \nu_1^2)^{1/2}.$$

The space elements normal to the orthogonal curvilinear coordinates μ, ν, ω are given as usual in the form :

$$\delta n'_\mu = a'\delta\mu\,[(\mu^2+\nu^2)/(1-\mu^2)]^{1/2} = \delta\mu/h'_\mu,$$
$$\delta n'_\nu = a'\delta\nu\,[(\mu^2+\nu^2)/(1+\nu^2)]^{1/2} = \delta\nu/h'_\nu,$$
$$\delta n'_\omega = a'\delta\omega\,[(1-\mu^2)\,(1+\nu^2)]^{1/2} = \delta\omega/h'_\omega.$$

Inverting the coordinates ρ', z' with respect to the origin, with radius of inversion $k=(aa')^{1/2}$, we have the new coordinates ρ, z given by

$$z = k^2 z'/r'^2, \quad \rho = k^2\rho'/r'^2, \quad r = (z^2+\rho^2)^{1/2}.$$

Hence

$$z, \rho = a\{(\mu\nu+\nu_1),$$
$$(1-\mu^2)^{1/2}(\nu^2+1)^{1/2}\}/\{1+\nu^2-\mu^2+\nu_1^2+2\mu\nu\nu_1\},$$

and the corresponding space elements normal to μ, ν, ω are given by

$$\delta n_\mu = \delta\mu/h_\mu, \quad \delta n_\nu = \delta\nu/h_\nu, \quad \delta n_\omega = \delta\omega/h_\omega,$$

with

$$h_\mu/h_{\mu'} = h_\nu/h_{\nu'} = h_\omega/h_{\omega'} = r'/r$$

as usual. The surfaces ξ or ν=constant are the inverses of the spheroids, and the surfaces η or μ=constant are the inverses of the hyperboloids. It will frequently be convenient to refer to "the surface ν_0" and "the inverse ν_0," meaning by these the spheroid $\nu=\nu_0$ and the inverse surface.

2. The solution of problems of electrostatics and hydrodynamics associated with a surface S requires, first, that suitable curvilinear coordinates should be available such that the surface S itself is given by χ=constant with χ one of the coordinates; next, that there should be general solutions of Laplace's equation in terms of these coordinates; and, lastly, that it should be possible to fit in the given boundary conditions on the surface S. The derivation of the inverse ν_0 surface from the spheroid at once gives the suitable curvilinear coordinates, since any surface and its inverse can be treated by means of the same coordinates *. The next requisite is also immediately available. For, as is well known, if V′ is a solution of Laplace's equation for coordinates $x'\ y'\ z'$, then

$$V = \frac{a}{r} V' = \frac{r'}{a'} V'$$

is a solution of Laplace's equation for the inverse coordinates x, y, z where a and a' are lengths associated with the two sets of coordinates and the radius of inversion is k, given by

$$k^2 = aa'.$$

Hence, if forms for V′ are available for the solution of problems associated with the spheroid ν_0, these same forms will yield a general form for V.

Now suppose V′ is a potential function suitable for the region including the sphere at infinity $r'=\infty$. Then for sufficiently large values of r'

$$V' = A_1 \frac{a'}{r'} + A_2 \left(\frac{a'}{r'}\right)^2 + \ldots .$$

Consequently

$$V = \frac{r'}{a'} V' = A_1 + A_2 \left(\frac{a'}{r'}\right) + A_3 \left(\frac{a'}{r'}\right)^2 + \ldots$$

for sufficiently large values of r' and for sufficiently small values of r, the identical series

$$V = A_1 + A_2 \left(\frac{r}{a}\right) + A_3 \left(\frac{r}{a}\right)^2 + \ldots,$$

since $\quad a'/r' = r/a.$

Hence V is not infinite at $r=0$.

* See Wrinch & Nicholson, Proc. Roy. Soc. (A), cviii. pp. 93–104 (1925).

Further, consider $\partial V/\partial r$ at $r=0$. We have

$$\frac{\partial V}{\partial r} = -\frac{h^2}{r^2}\frac{\partial}{\partial r'}(r'V') = -\frac{r'^2}{k^2}\frac{\partial}{\partial r'}(r'V'),$$

and for sufficiently large values of r'

$$\frac{\partial V}{\partial r} = \frac{r'^2}{k^2}\left\{A_1\frac{a'}{r'^2} + 2A_2\frac{a'^2}{r'^3}\cdots\right\},$$

and for sufficiently small values of r

$$\frac{\partial V}{\partial r} = \frac{1}{a}\left\{A_1 + 2A_2\left(\frac{r}{a}\right) + 3A_3\left(\frac{r}{a}\right)^2 + \ldots\right\},$$

and V is therefore not infinite at $r=0$.

Hence V and all its derivatives are finite at $r=0$, provided that V′ is a suitable potential for a region including the sphere at infinity $r'=\infty$. And in the same way, V and all its derivatives are finite on $r=\infty$, provided that V′ is a suitable potential for a region including the point $r'=0$.

It is well known * that for the space outside the spheroid ν_0 we can take

$$V' = \Sigma\Sigma\, a_{m,n}\, P_m^n(\mu)\, q_m^n(\nu)\cos n(\omega+\omega_n) \quad . \quad . \quad (1)$$

(the function $q_m^n(\nu)$ being defined after Lamb), since on the sphere at infinity $\nu=\infty$, $q_m^n(\nu)$ tends to zero. Similarly, for the space inside we can take

$$V' = \Sigma\Sigma\, a_{m,n}\, P_m^n(\mu)\, p_m^n(\nu)\cos n(\omega+\omega_m) \quad . \quad . \quad . \quad (2)$$

Hence the forms of potential function

$$V = \left(\frac{a}{r},\ \frac{r'}{a'}\right)\Sigma\Sigma\, a_{m,n}\, P_m^n(\mu)\,[q_m^n(\nu),\ p_m^n(\nu)]\cos n(\omega+\omega_m)$$

$$\ldots \quad (3)$$

are available for problems associated with the inverse ν_0, the form containing $q_m^n(\nu)$ being appropriate to the region corresponding to the outside of the spheroid ν_0, and the form containing $p_m^n(\nu)$ to the region corresponding to the inside of the spheroid ν_0.

As we shall be concerned wholly with problems in which there is symmetry about the z-axis, it will only be necessary to use the potential function in the forms :

$$V' = \Sigma\, a_m\, P_m(\mu)\,\{q_m(\nu),\ p_m(\nu)\}.$$

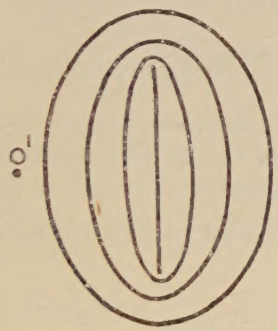
* See Lamb, 'Hydrodynamics' (1924); also Nicholson, Trans. Roy. Soc. (A), ccxiv. pp. 49-93 (1924), where many properties of the function $q_n(\nu)$ are discussed.

The third and only remaining point is to fit the general potential suitably selected from (3) to the boundary condition to be satisfied on the inverse ν_0. And this part of the problem will be discussed separately in each case.

I. *Problems associated with the Bean-Shaped Surfaces.*

1·1. We will consider first the problems associated with the inverse surface when $\nu_0 < \nu_1$. In this case the origin—which is the centre of inversion—is exterior to the surface ν_0, and the inverse ν_0 is therefore of the "bean" type. Fig. 1

Fig. 1.



shows a set of confocal oblate spheroids exterior to a centre of inversion O′ and fig. 2 their inverses with respect to this centre of inversion. Since the centre of inversion is exterior to the spheroid ν_0, therefore regions outside the spheroid ν_0 and the inverse ν_0 correspond, and the regions inside also correspond. Thus the suitable form of potential outside and inside the inverse ν_0 are given by

$$V_{out} = \left(\frac{a}{r}, \frac{r'}{a'}\right) \Sigma a_m P_m(\mu) q_m(\nu),$$

$$V_{in} = \left(\frac{a}{r}, \frac{r'}{a'}\right) \Sigma b_m P_m(\mu) p_m(\nu).$$

1·2. *The Freely-charged Conductor.*

The first problem to consider is that of the inverse ν_0 freely charged with electricity to potential V_0. Then

$$V = \left(\frac{a}{r}, \frac{r'}{a'}\right) \Sigma a_m P_m(\mu) q_m(\nu).$$

On $\nu=\nu_0$ we have to satisfy the boundary condition $V=V_0$. Thus the coefficients a_m have to be chosen in such a way that on $\nu=\nu_0$

$$V\left(\frac{r}{a}, \frac{a'}{r'}\right) = \Sigma a_m P_m(\mu)\, q_m(\nu).$$

We therefore require the expansion of

$$\frac{r}{a}=\frac{a'}{r'} = (\nu^2-\mu^2+1+2\mu\nu\nu_1+\nu_1^2)^{-1/2}$$

in a series of $P_m(\mu)$ functions.

Now it is known * that

$$(\nu^2-\mu^2+1+2\mu\nu\nu_1+\nu_1^2)^{-1/2}$$
$$= \sum_0^\infty (-)^m(2m+1)\,[q_n(\nu_1)\,p_n(\nu),\ p_n(\nu_1)\,q_n(\nu)]\,P_n(\mu), \quad (4)$$

according as $\nu_1 \gtrless \nu$. Since we have to apply the condition $V=V_0$ on $\nu=\nu_0<\nu_1$, we use the expansion of a'/r' suitable for $\nu=\nu_0$, and in consequence we deduce that

$$a_m\, q_m(\nu_0) = V_0(-)^m(2m+1)\, q_m(\nu_1)\, P_m(\nu_0).$$

Therefore

$$V = \left(\frac{a}{r}, \frac{r'}{a'}\right) V_0 \sum_0^\infty (-)^m(2m+1)\frac{q_m(\nu_1)\,P_m(\nu_0)}{q_m(\nu_0)}\, q_m(\nu)\, P_m(\mu).$$

To find the charge E on the inverse ν_0 we have

$$E = \operatorname*{lt}_{r\to\infty} (rV),$$

and $r=\infty$ when $r'=0$; and this is the case when $\mu=-1$, $\nu=\nu_1$. Thus

$$E = \operatorname*{lt}_{\mu=-1,\ \nu=\nu_1} (rV)$$
$$= aV_0 \sum_0^\infty (-)^m(2m+1)\frac{q_m(\nu_1)\,p_m(\nu_0)}{q_m(\nu_0)}\, q_m(\nu_1)\, P_m(-1)$$
$$= aV_0 \sum_0^\infty (2m+1)\, q_m^2(\nu_1)\, p_m(\nu_0)/q_m(\nu_0).$$

The capacity C then stands in the form

$$C = E/V_0 = a \sum_0^\infty (2m+1)\, q_m^2(\nu_1)\, p_m(\nu_0)/q_m(\nu_0).$$

* Nicholson, *loc. cit.* p. 57.

The surface density σ at any point μ on the inverse ν_0 is given by

$$4\pi\sigma = -(h_\nu\, \partial V/\partial\nu)\nu=\nu_0.$$

Now

$$\left(\frac{\partial V}{\partial \nu}\right)_{\nu=\nu_0} = \left(\frac{1}{r}\frac{\partial}{\partial\nu}(rV - rV_0)\right)_{\nu=\nu_0}$$

$$= \left\{\frac{1}{r}\frac{\partial}{\partial\nu} aV_0 \sum_0^\infty (-)^m(2m+1)\, q_m(\nu_1) \right.$$

$$\left. \times \left\{\frac{p_m(\nu_0)}{q_m(\nu_0)} q_m(\nu) - p_m(\nu)\right\} P_m(\mu)\right\}_{\nu=\nu_0}$$

$$= \left(\frac{aV_0}{r}\right)_{\nu=\nu_0} \sum_0^\infty (-)^m(2m+1)\, q_m(\nu_1)$$

$$\times \left\{\frac{p_m(\nu_0)}{q_m(\nu_0)} q_m'(\nu_0) - p_m'(\nu_0)\right\} P_m(\mu).$$

Also

$$h_\nu = \frac{r'}{r} h_\nu' = \frac{r'}{ra'}\left(\frac{1+\nu^2}{\mu^2+\nu^2}\right)^{1/2} = \frac{a}{r^2}\left(\frac{1+\nu^2}{\mu^2+\nu^2}\right)^{1/2}.$$

Hence

$$4\pi\sigma = -\left(\frac{a^2V_0}{r^3}\frac{1+\nu^2}{\mu^2+\nu^2}\right)_{\nu=\nu_0} \sum_0^\infty (-)^m(2m+1)\, q_m(\nu_1)$$

$$\times \left\{\frac{p_m(\nu_0)}{q_m(\nu_0)} q_m'(\nu_0) - p_m'(\nu_0)\right\} P_m(\mu)$$

$$= -\frac{V_0(1+\nu_0^2)^{1/2}(\nu_0^2 - \mu^2 + 1 + 2\mu\nu_0\nu_1 + \nu_1^2)^{3/2}}{a(\mu^2+\nu_0^2)^{1/2}}$$

$$\times \sum_0^\infty (-)^m(2m+1)\, q_m(\nu_1)$$

$$\times \left\{\frac{p_m(\nu_0)}{q_m(\nu_0)} q_m'(\nu_0) - p_m'(\nu_0)\right\} P_m(\mu).$$

Thus the surface density depends on the series

$$S(\nu_0) = \sum_0^\infty (-)^m(2m+1)\, q_m(\nu_1)\frac{p_m(\nu_0)}{q_m(\nu_0)} q_m'(\nu_0)\, P_m(\mu) \quad (\nu_0 < \nu_1), \qquad \ldots \quad (5)$$

which yields convenient approximations when ν_0/ν_1 is small, and on the series

$$-\frac{\partial}{\partial\nu_0}\sum_0^\infty (-)^m(2m+1)\, q_m(\nu_1)\, p_m(\nu_0)\, P_m(\mu)$$

$$= -\frac{\partial}{\partial\nu_0}(\nu_0^2 + 1 - \mu^2 + 2\mu\nu_0\nu_1 + \nu_1^2)^{-1/2}$$

$$= (\nu_0 + \mu\nu_1)/(\nu_0^2 + 1 - \mu^2 + 2\mu\nu_0\nu_1 + \nu_1^2)^{3/2}.$$

It is also worth while to record the result in the form

$$4\pi\sigma = \frac{V_0(\nu_0^2-\mu^2+1+2\mu\nu_0\nu_1+\nu_1^2)^{3/2}}{a(\mu^2+\nu_0^2)^{1/2}(1+\nu_0^2)^{1/2}} \times \sum_0^\infty (-)^m(2m+1)\frac{q_m(\nu_1)}{q_m(\nu_0)}\,P_n(\mu),$$

which also follows in view of the fact that

$$p_m'(\nu)\,q_m(\nu)-q_m'(\nu)\,p_m(\nu) = 1/(1+\nu^2)$$

after the usual manner for functions sharing the same linear differential equation of the second order.

1·3. *The Earthed Conductor in a Uniform Field parallel to the Axis of Figure.*

Suppose the conductor is placed in a uniform field of force given by

$$V_0 = fz,$$

and let the potential due to the conductor be V. Then the potential of the field in the presence of the conductor $(V+V_0)$ must be zero on the surface $\nu=\nu_0$, and, in addition, V must be evanescent as $r\to\infty$ and must have no singularities outside the conductor. Thus we assume the form :

$$V = \frac{a}{r}\sum_0^\infty A_n\,q_n(\nu)\,P_n(\mu).$$

Now, on $\nu=\nu_0$ the boundary condition to be satisfied is that

$$-V = fz = fa(\mu\nu+\nu_1)/\{1+\nu^2-\mu^2+\nu_1^2+2\mu\nu\nu_1\},$$

or that

$$-\frac{Vr}{a^2} = \frac{f(\mu\nu+\nu_1)}{(1+\nu^2-\mu^2+\nu_1^2+2\mu\nu\nu_1)^{3/2}} = -f\frac{\partial}{\partial\nu_1}(1+\nu^2-\mu^2+\nu_1^2+2\mu\nu\nu_1)^{-1/2}.$$

To apply the boundary condition on $\nu=\nu_0$ we therefore use the fact that

$$\frac{\partial}{\partial\nu_1}(1+\nu^2-\mu^2+\nu_1^2+2\mu\nu\nu_1)^{-1/2} = \sum_0^\infty(-)(2m+1)\,q_m'(\nu_1)\,p_m(\nu)P_m(\mu),$$

which is deduced from (4) ; and then it follows that

$$A_m\,q_m(\nu_0) = fa(-)^m(2m+1)\,q_m'(\nu_1)\,p_m(\nu_0)\,;$$

so that

$$V = \frac{fa^2}{r}\sum_0^\infty(-)^m(2m+1)\frac{q_m'(\nu_1)\,p_m(\nu_0)}{q_m(\nu_0)}q_m(\nu)\,P_m(\mu)$$

and

$$V+V_0=\frac{fa^2}{r}\sum_0^\infty(-)^m(2m+1)\,q_m'(\nu_1)\times\left\{\frac{p_m(\nu_0)}{q_m(\nu_0)}q_m(\nu)-p_m(\nu)\right\}P_m(\mu).$$

The charge induced on the conductor, E, is given by

$$E=\operatorname*{lt}_{r\to\infty}(Vr)=\operatorname*{lt}_{\mu=-1,\ \nu=\nu_1}(Vr)$$
$$=fa^2\sum_0^\infty(2m+1)\,q_m'(\nu_1)\,p_m(\nu_0)\,q_m(\nu_1)/q_m(\nu_0).$$

The surface density may also be found. We have

$$4\pi\sigma=-\left[h_\nu\,\partial(V+V_0)/\partial\nu\right]_{\nu=\nu_0}$$

and

$$\left(\frac{\partial}{\partial\nu}(V+V_0)\right)_{\nu=\nu_0}=\left[\frac{1}{r}\frac{\partial}{\partial\nu}(rV+rV_0)\right]_{\nu=\nu_0}$$
$$=\frac{fa^2}{r}\sum_0^\infty(-)^m(2m+1)\,q_m'(\nu_1)\times\left\{\frac{p_m(\nu_0)}{q_m(\nu_0)}q_m'(\nu_0)-p_m'(\nu_0)\right\}P_m(\mu),$$

and

$$4\pi\sigma=-\left[\frac{fa^3}{r^3}\left(\frac{1+\nu^2}{\mu^2+\nu^2}\right)^{1/2}\right]_{\nu=\nu_0}\sum_0^\infty(-)^m(2m+1)\,q_m'(\nu_1)\times\left\{\frac{p_m(\nu_0)}{q_m(\nu_0)}q_m'(\nu_0)-p_m'(\nu_0)\right\}P_m(\mu)$$
$$=-\frac{f(1+\nu_0^2)^{1/2}(\nu_0^2-\mu^2+1+2\mu\nu_0\nu_1+\nu_1^2)^{3/2}}{(\mu^2+\nu_0^2)^{1/2}}\times\sum_0^\infty(-)^m(2m+1)\,q_m'(\nu_1)\times\left\{\frac{p_m(\nu_0)}{q_m(\nu_0)}q_m'(\nu_0)-p_m'(\nu_0)\right\}P_m(\mu)$$
$$=-\frac{f(1+\nu_0^2)^{1/2}(\nu_0^2-\mu^2+1+2\mu\nu_0\nu_1+\nu_1^2)^{3/2}}{(\mu^2+\nu_0^2)^{1/2}}\times\left\{\frac{\partial S}{\partial\nu_1}+\frac{\partial}{\partial\nu_1}\frac{\nu_0+\mu\nu_1}{(\nu_0^2+1-\mu^2+2\mu\nu_0\nu_1+\nu_1^2)^{3/2}}\right\}$$
$$=+\frac{f(\nu_0^2-\mu^2+1+2\mu\nu_0\nu_1+\nu_1^2)^{3/2}}{(\mu^2+\nu_0^2)^{1/2}(1+\nu_0^2)^{1/2}}\times\sum_0^\infty(-)^m(2m+1)\frac{q_m'(\nu_1)}{q_m(\nu_0)}P_m(\mu).$$

II. *Problems associated with the Spherical Bowl.*

2·1. The particular case when $\nu_0=0$ is of special interest. The spheroid ν_0 then becomes the circular disk of radius a', and the centre of inversion is on the line through the centre perpendicular to its plane at a distance $-a'\nu_1$ from it.

The inverse ν_0 is therefore the spherical bowl *, given by

$$z=\frac{a\nu_1}{1-\mu^2+\nu_1^2}, \qquad \rho=\frac{a(1-\mu^2)^{1/2}}{1-\mu^2+\nu_1^2},$$

which is part of the sphere,

$$\rho^2+z(z-a/\nu_1)=0,$$

which passes through the origin $\rho=z=0$. The parameters associated with the spherical bowl are a and ν_1. These may be expressed in terms of f, the diameter of the sphere of which it forms part, and 2β, the angle it subtends at the origin O, by the relations

$$\nu_1=\cot\beta, \qquad a=f\cot\beta.$$

Any point on the bowl may be specified by μ, or, more conveniently, by r the radius vector from O. Thus

$$r=\frac{a}{(1-\mu^2+\nu_1^2)^{1/2}}=\frac{f\cot\beta}{(\operatorname{cosec}^2\beta-\mu^2)^{1/2}}=\frac{f\cos\beta}{(1-\mu^2\sin^2\beta)^{1/2}},$$

and therefore

$$\mu^2=\operatorname{cosec}^2\beta\left(1-\frac{f^2}{r^2}\cos^2\beta\right).$$

It is sometimes convenient to use, instead of the parameter β, c the minimum length of r on the bowl. We then have

$$c=f\cos\beta,$$

and in consequence

$$r=\frac{c}{(1-\mu^2+\mu^2c^2/f^2)^{1/2}}, \qquad \mu^2=\frac{f^2}{f^2-c^2}\left(1-\frac{c^2}{r^2}\right)$$

and

$$\nu_1=\frac{c}{(f^2-c)^{1/2}}, \qquad a=\frac{fc}{(f^2-c^2)^{1/2}}.$$

* Problems associated with the spherical bowl have been treated by a number of writers, including the following :—Kelvin, 'Papers on Electrostatics and Magnetism,' xv. (1884) (papers dated January 1869); Ferrers Quart. J. of Math. xviii. pp. 97–109 (1882); Gallop, Quart. J. of Math. xxi. pp. 229–256 (1886).

Fig. 2.

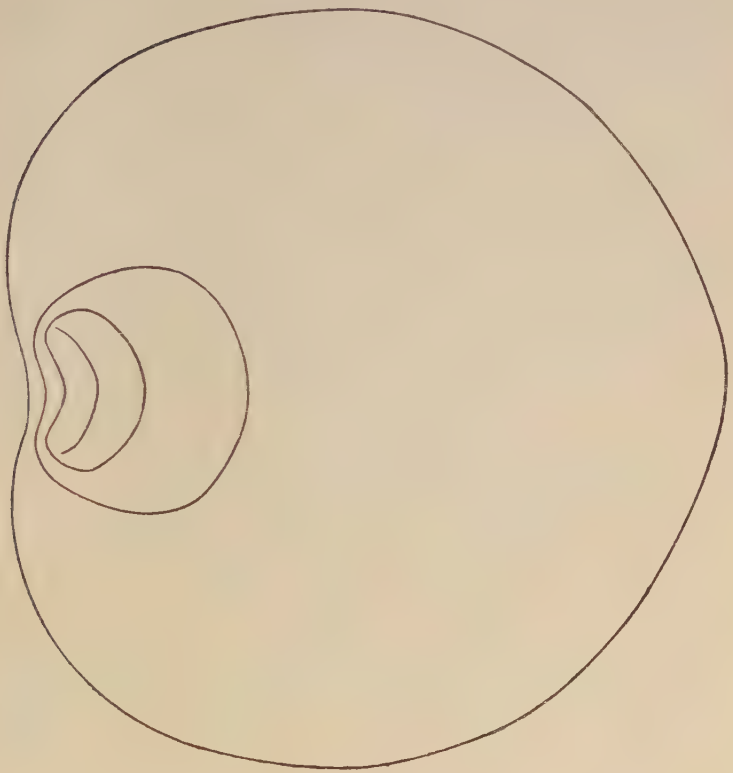
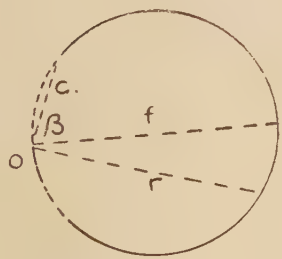


Fig. 3.

The Disk.

Fig. 4.



The Spherical Bowl.

2·2. *The Freely-charged Conductor.*

We consider first the problem of the conducting spherical bowl freely electrified to potential V_0. Then merely putting $\nu_0=0$, we have the following results:

$$V = \frac{2a}{\pi r} V_0 \sum_0^\infty (4n+1)\, q_{2n}(\nu_1)\, q_n(\nu)\, P_m(\mu),$$

since

$$p_{2n}(0)/q_{2n}(0) = \frac{2}{\pi}, \qquad p_{2n+1}(0) = 0.$$

Next

$$E = \frac{2}{\pi} a V_0 \sum_0^\infty (4n+1)\, q_{2n}^2(\nu_1),$$

$$C = \frac{2a}{\pi} \Sigma (4n+1)\, q_{2n}^2(\nu_1),$$

which by a formula due to Nicholson * reduces to

$$C = \frac{E}{V_0} = \frac{a}{2\pi} \left\{ \frac{\cot^{-1}(\nu_1)}{\nu_1} + \frac{1}{1+\nu_1^2} \right\}$$

$$= \frac{f}{2\pi} \{2\beta + \sin 2\beta\},$$

the well-known result obtained by Kelvin (see footnote, p. 874).

Further, for μ positive,

$$4\pi\sigma = -\frac{V_0(1-\mu^2+\nu_1^2)^{3/2}}{a\mu} \left[S(0) + \frac{\mu\nu_1}{(1-\mu^2+\nu_1^2)^{3/2}} \right],$$

where

$$S(0) = \sum_0^\infty (-)^m (2m+1)\, q_m(\nu_1) \frac{p_m(0)}{q_m(0)}\, q_m'(0)\, P_m(\mu)$$

$$= \frac{2}{\pi} \sum_0^\infty (4n+1)\, q_{2n}(\nu_1)\, q_{2n}'(0)\, P_{2n}(\mu)$$

$$= -\frac{2\mu\nu_1}{\pi(1-\mu^2+\nu_1^2)^{3/2}} \left\{ \frac{\pi}{2} + \frac{(1-\mu^2+\nu_1^2)^{1/2}}{\mu} - \tan^{-1} \frac{(1-\mu^2+\nu_1^2)^{1/2}}{\mu} \right\}$$

* *Loc. cit.* p. 64.

by a formula due to Nicholson *. Thus, when $\mu > 0$,

$$4\pi\sigma = \frac{2V_0\nu_1}{\pi a}\left\{\frac{(1-\mu^2+\nu_1^2)^{1/2}}{\mu} - \tan^{-1}\frac{(1-\mu^2+\nu_1^2)^{1/2}}{\mu}\right\}$$
$$= \frac{2V_0}{\pi f}\left\{\frac{a}{\mu r} - \tan^{-1}\frac{a}{\mu r}\right\}$$
$$= \frac{2V_0}{\pi f}\left\{\frac{c}{(r^2-c^2)^{1/2}} - \tan^{-1}\frac{c}{(r^2-c^2)^{1/2}}\right\}.$$

Further, when $\mu < 0$,

$$4\pi\sigma = + \frac{V_0(1-\mu^2+\nu_1^2)^{3/2}}{a\mu}\left[S(0) + \frac{\mu\nu_1}{(1-\mu^2+\nu_1^2)^{3/2}}\right].$$

Now consider the point given by μ when μ is positive. It is on the inside of the spherical bowl. Then at the specific point given by $-\mu$ outside and $+\mu$ inside we have

$$4\pi(\sigma_{\text{outside}} - \sigma_{\text{inside}})$$
$$= -\frac{V_0(1-\mu^2+\nu_1^2)^{3/2}}{a\mu}\left[S(0,-\mu) - \frac{\mu\nu_1}{(1-\mu^2+\nu_1^2)^{3/2}}\right]$$
$$+ \frac{V_0(1-\mu^2+\nu_1^2)^{3/2}}{a\mu}\left[S(0,\mu) + \frac{\mu\nu_1}{(1-\mu^2+\nu_1^2)^{3/2}}\right]$$
$$= \frac{2V_0\nu_1}{a} = \frac{2V_0}{f},$$

since S is an even function of μ. And the densities inside and outside the spherical bowl at any point are completely specified by this result and the result which may be written

$$4\pi\sigma_{\text{inside}} = \frac{2V_0}{\pi f}\left(\frac{c}{(r^2-c^2)^{1/2}} - \tan^{-1}\frac{c}{(r^2-c^2)^{1/2}}\right),$$

agreeing with Kelvin's result.

2·3. *The Earthed Conductor in a Uniform Field parallel to the Axis of Figure.*

The results in the case when the conducting spherical bowl is earthed in the presence of the external field

$$V_0 = Cz/a$$

may also be written down. If V is the potential thrown out by the bowl, and in consequence $V + V_0$ the complete potential of the field,

$$V + V_0$$
$$= \frac{Ca}{r}\sum_0^\infty (-)^m(2m+1)\,q_m'(\nu_1)\left[\frac{p_m(0)}{q_m(0)}\,q_m(\nu) - p_m(\nu)\right]P_m(\mu).$$

* *Loc. cit.* p. 84.

Further, for μ positive,

$$4\pi\sigma = -\frac{C(1-\mu^2+\nu_1^2)^{3/2}}{a\mu}\left\{\frac{\partial}{\partial\nu_1}S(0)+\frac{\partial}{\partial\nu_1}\frac{\mu\nu_1}{(1-\mu^2+\nu_1^2)^{3/2}}\right\}$$

$$= -\frac{C(1-\mu^2+\nu_1^2)^{3/2}}{a\mu}\left\{\frac{\partial}{\partial\nu_1}S(0)+\frac{\mu}{(1-\mu^2+\nu_1^2)^{3/2}} - \frac{3\mu\nu_1^2}{(1-\mu^2+\nu_1^2)^{5/2}}\right\}.$$

Similarly for μ negative

$$4\pi\sigma = +\frac{C(1-\mu^2+\nu_1^2)^{3/2}}{a\mu}\left\{\frac{\partial}{\partial\nu_1}S(0)+\frac{\mu}{(1-\mu^2+\nu_1^2)^{3/2}} - \frac{3\mu\nu_1^2}{(1-\mu^2+\nu_1^2)^{5/2}}\right\},$$

and therefore at a point on the spherical bowl given by μ on the inside and $-\mu$ on the outside,

$$4\pi(\sigma_{\text{outside}}-\sigma_{\text{inside}})$$

$$= +\frac{2C(1-\mu^2\times\nu_1^2)^{3/2}}{a\mu}\cdot\left\{\frac{\mu}{(1-\mu^2+\nu_1^2)^{3/2}}-\frac{3\mu\nu_1^2}{(1-\mu^2+\nu_1^2)^{5/2}}\right\}$$

$$= \frac{2C}{a}\left(1-\frac{3\nu_1^2}{1-\mu^2+\nu_1^2}\right)=\frac{2C}{a}\left(1-\frac{3r^2}{f^2}\right),$$

since $\partial S/\partial\nu_1$ is an even function of μ.

It remains to evaluate $\partial S/\partial\nu_1$ when μ is positive.

Differentiating the expression for S, we have

$$\frac{\partial S}{\partial\nu_1} = \left\{-\frac{2\mu}{\pi(1-\mu^2+\nu_1^2)^{3/2}}+\frac{6\mu\nu_1^2}{\pi(1-\mu^2+\nu_1^2)^{5/2}}\right\} \times\left\{\frac{\pi}{2}+\frac{(1-\mu^2+\nu_1^2)^{1/2}}{\mu}-\tan^{-1}\frac{(1-\mu^2+\nu_1^2)^{1/2}}{\mu}\right\}$$

$$-\frac{2\mu\nu_1}{\pi(1-\mu^2+\nu_1^2)^{3/2}}\left\{\frac{\nu_1}{(\mu1-\mu^2+\nu_1^2)^{1/2}}\cdot\frac{1-\mu^2+\nu_1^2}{1+\nu_1^2}\right\}$$

$$= \left[-\frac{\mu}{(1-\mu^2+\nu_1^2)^{3/2}}+\frac{3\mu\nu_1^2}{(1-\mu^2+\nu_1^2)^{5/2}}\right] \times\left[1-\frac{2}{\pi}\tan^{-1}\frac{(1-\mu^2+\nu_1^2)^{1/2}}{\mu}\right]$$

$$+\frac{2}{\pi}\left\{-\frac{1}{1-\mu^2+\nu_1^2}+\frac{3\nu_1^2}{(1-\mu^2+\nu_1^2)^2} - \frac{\nu_1^2}{(1-\mu^2+\nu_1^2)(1+\nu_1^2)}\right\}.$$

Hence for μ positive, namely at a point inside the bowl,

$$4\pi\sigma_{\text{inside}} = -\frac{C}{a\mu}(1-\mu^2+\nu_1^2)^{2/3}\left\{\frac{\partial}{\partial\nu_1}S(0) + \frac{\mu}{(1-\mu^2+\nu_1^2)^{3/2}} - \frac{3\mu\nu_1^2}{(1-\mu^2+\nu_1^2)^{5/2}}\right\}$$

$$= -\frac{2C}{\pi a}\left(1-\frac{3\nu_1^2}{1-\mu^2+\nu_1^2}\right)\tan^{-1}\frac{(1-\mu^2+\nu_1^2)^{1/2}}{\mu} + \frac{2C}{\pi a\mu}\left\{\frac{a}{r}-\frac{3ra}{f^2}+\frac{a^2r}{f^2(a^2+\mu^2\nu^2)}\right\}$$

$$= -\frac{2C}{\pi a}\left(1-\frac{3r^2}{f^2}\right)\tan^{-1}\frac{a}{\mu r} + \frac{2C}{\pi\mu r}\left[1-\frac{3r^2}{f^2}+\frac{a^2r^2}{f^2(a^2+\mu^2r^2)}\right]$$

$$= -\frac{2C/a}{\pi}\left\{\left(1-\frac{3r^2}{f^2}\right)\tan^{-1}\frac{c}{(r^2-c^2)^{1/2}} - \frac{c}{(r^2-c^2)^{1/2}}\left(1-\frac{3r^2}{f^2}+\frac{c^2}{f^2}\right)\right\}.$$

The densities are then completely determined by the equations. It will be remembered that as $c\to 0$, $\sigma_{\text{inside}}\to 0$ and $\sigma_{\text{outside}}-\sigma_{\text{inside}}$ remains unchanged, so that

$$4\pi\sigma_{\text{outside}} = \frac{2C}{a}\left(1-\frac{3r^2}{f^2}\right), \qquad \sigma_{\text{inside}} = 0$$

in accordance with the usual result for a sphere of radius $\frac{1}{2}f$ with its centre at $(0, 0, \frac{1}{2}f)$ earthed in a uniform field of force

$$V_0 = Cz/a.$$

III. *Problems associated with the Ovoid Surface.*

3·1. The case when the centre of inversion lies within the spheroid ν_0, given by $\nu_1 < \nu_0$, can be discussed on the same lines.

Confocal oblate spheroids which lie outside the centre of

Fig. 5.

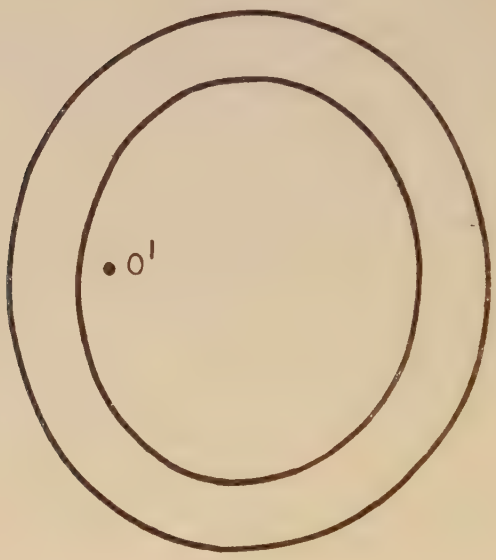
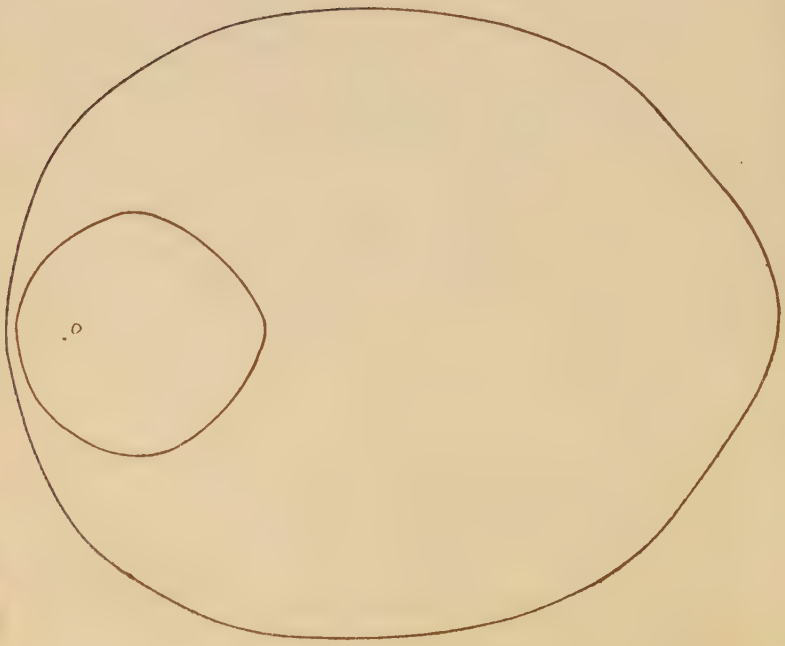


Fig. 6.



inversion O′ are shown in fig. 5. The inverse surface ν_0 is now of the ovoid type, and is shown in fig. 6. And evidently the region inside the spheroid ν_0 now corresponds to the region outside the inverse ν_0. Both problems—of the conductor in the form of the inverse ν_0, freely charged and earthed in a uniform field of force—require a potential of the form

$$V = \left(\frac{a}{r}, \frac{r'}{a'}\right) \Sigma A_m P_m(\mu) p_m(\nu).$$

A closely similar procedure to that given in § 1 can by followed. It will be sufficient merely to record the results.

3·2. *The Freely-charged Conductor.*

The potential when the conductor in the form of the inverse ν_0 is charged to potential V_0, is given by

$$V = \left(\frac{a}{r}, \frac{r'}{a'}\right) V_0 \sum_0^\infty (-)^m (2m+1) \frac{p_m(\nu_1)\, q_m(\nu_0)}{p_m(\nu_0)} p_m(\nu)\, P_m(\mu).$$

The charge E and the capacity C are given by

$$C = \frac{E}{V_0} = a \sum_0^\infty (2m+1)\, p_m^2(\nu_1)\, q_m(\nu_0)/p_m(\nu_0).$$

Further,

$$4\pi\sigma = (|h_\nu| \partial V/\partial \nu)_{\nu=\nu_0},$$

since ν is now decreasing on the outgoing normal to the inverse ν_0. Thus

$$4\pi\sigma = \frac{V_0(\nu_0^2 - \mu^2 + 1 + 2\mu\nu_0\nu_1 + \nu_1^2)^{3/2}}{a(\mu^2+\nu_0^2)^{1/2}} (1+\nu_0^2)^{1/2}$$

$$\times \sum_0^\infty (-)^m (2m+1)\, p_m(\nu_1)$$

$$\times \left\{ \frac{q_m(\nu_0)}{p_m(\nu_0)} p_m'(\nu_0) - q_m'(\nu_0) \right\} P_m(\mu)$$

$$= \frac{V_0(\nu_0^2 - \mu^2 + 1 + 2\mu\nu_0\nu_1 + \nu_1^2)^{3/2}}{a(\mu^2+\nu_0^2)^{1/2}(1+\nu_0^2)^{1/2}}$$

$$\times \sum_0^\infty (-)^m (2m+1) \frac{p_m(\nu_1)}{p_m(\nu_0)} P_m(\mu).$$

Thus the surface density depends on the series

$$T(\nu_0) = \sum_0^\infty (-)^m (2m+1)\, p_m(\nu_1) \frac{q_m(\nu_0)}{p_m(\nu_0)} p_m'(\nu_0)\, P_m(\mu) \qquad \nu_1 < \nu_0, \quad . \quad . \quad . \quad (6)$$

which is continuous at $\nu_0 = \nu_1$ with the series $S(\nu_0)$ required in the case of the bean-shaped surfaces, and the series

$$-\frac{\partial}{\partial \nu_0} \sum_0^\infty (-)^m (2m+1)\, p_m(\nu_1)\, q_m(\nu_0)\, P_m(\mu)$$
$$= (\nu_0 + \mu\nu_1) / (\nu_0^2 + 1 - \mu^2 + 2\mu\nu_0\nu_1 + \nu_1^2)^{3/2}$$

as before.

It will be noticed that the case $\nu_0 = \infty$ affords a minor verification. In that case the inverse ν_0 becomes a sphere of radius a/ν_0, and

$$C = \frac{E}{V_0} = \frac{a}{\nu_0},$$

neglecting $(1/\nu_0)^2$, and

$$4\pi\sigma = \frac{V_0 \nu_0^3}{a} \left[T(\infty) + \frac{1}{\nu_0^2} \right]$$
$$= \frac{V_0 \nu_0}{a} = \frac{E}{(a/\nu_0)^2}$$

as usual.

3·3. *The Earthed Conductor in a Uniform Field parallel to the Axis of Figure.*

The uniform field is given by

$$V_0 = fz.$$

Then V, the potential thrown out by a conductor in the form of the inverse ν_0, is given by

$$V = \frac{fa^2}{r} \sum_0^\infty (-)^m (2m+1) \frac{p_m'(\nu_1)\, q_m(\nu_0)}{p_m(\nu_0)} p_m(\nu)\, P_m(\mu),$$

and the total potential is

$$V + V_0 = \frac{fa^2}{r} \sum_0^\infty (-)^m (2m+1)\, p_m'(\nu_1) \left\{ \frac{q_m(\nu_0)}{p_m(\nu_0)} p_m(\nu) - q_m(\nu) \right\} P_m(\mu).$$

Then E, the charge on the conductor, is

$$E = fa^2 \sum_0^\infty (2m+1)\, p_m'(\nu_1)\, q_m(\nu_0)\, p_m(\nu_1)/p_m(\nu_0).$$

Also

$$4\pi\sigma = \frac{f(1+\nu_0^2)^{1/2}(\nu_0^2-\mu^2+1+2\mu\nu\nu_0+\nu_1^2)^{3/2}}{(\mu^2+\nu_0^2)^{1,2}} \sum_0^\infty (-)^m(2m+1)$$

$$\times p_m'(\nu_1)\left\{\frac{q_m(\nu_0)}{p_m(\nu_0)}p_m'(\nu_0)-q_m'(\nu_0)\right\} \mathrm{P}_m(\mu)$$

$$= \frac{f(1+\nu_0^2)^{1/2}(\nu_0^2-\mu^2+1+2\mu\nu_0\nu_1+\nu_1^2)^{3/2}}{(\mu^2+\nu_0^2)^{1,2}}$$

$$\times\left\{\frac{\partial \mathrm{T}}{\partial\nu_1}+\frac{\partial}{\partial\nu_1}\frac{\nu_0+\mu\nu_1}{(\nu_0^2+1-\mu^2+2\mu\nu_0\nu_1+\nu_1^2)^{3,2}}\right\}$$

$$= \frac{f(\nu_0^2-\mu^2+1+2\mu\nu_0\nu_1+\nu_1^2)^{3/2}}{(\mu^2+\nu_0^2)^{1/2}(1+\nu_0^2)^{1/2}} \sum_0^\infty (-)^m(2m+1)$$

$$\times\frac{p_m'(\nu_1)}{p_m(\nu_0)}\mathrm{P}_m(\mu).$$

It will be noticed that the various series involved in both problems are convergent since $\nu_1<\nu_0$, and approximations may readily be obtained to any desired order when ν_1/ν_0 is sufficiently small.

3·4. The case when $\nu_0\to\infty$ again affords a minor verification. The inverse surface ν_0 is then a sphere of radius a/ν_0 with its centre at the point $z=-a\nu_1/\nu_0^2$, higher powers of $1/\nu_0$ being neglected. The results in this case become

$$\mathrm{E} = fa^2\{3q_1(\nu_0)\nu_1/\nu_0+\ldots\} = \mathrm{O}(1/\nu_0^3),$$

$$4\pi\sigma = f\nu_0\{-3\mu/\nu_0+\ldots\} = -3\mu f+\mathrm{O}(1/\nu_0),$$

in accordance with the usual theory.

LXXXV. *The Absolute Zero of the Externally Controllable Entropy and Internal Energy of a Substance and a Mixture.* *By* Prof. R. D. Kleeman, *D.Sc., Consulting and Research Physicist and Physical Chemist, Associate Professor of Physics, Union College, Schenectady, N.Y.**

THE properties of the internal energy and entropy of a substance at the absolute zero of temperature and the connexion of these properties with those at higher temperatures, has recently attracted a considerable amount of attention, and given rise to a good deal of experimental research. The importance of the subject was probably firs

* Communicated by the Author.

recognized by Nernst, who enunciated his well-known heat theorem in this connexion. The development of the subject ultimately resulted in a theorem which is often called the Third Law of Thermodynamics. The object of this paper is to show that these results are only cases of a much more general result, which can be deduced directly from results of an axiomatic character.

1. *The Division of the Internal Energy and Entropy into Two Parts.*

The internal energy of a substance or mixture of given mass may be divided into two parts, one of which is a function of the variables temperature and volume only, while the remaining part is independent of these quantities. The first part would accordingly be externally controllable, while this would not be the case with the other part, and hence these two parts will be called the externally controllable and externally uncontrollable energies of the system. The heat absorbed when the temperature of a substance is increased, or its volume is isothermally increased, are examples of changes in the controllable internal energy of a system. Changes in the uncontrollable internal energy would evidently be spontaneous. An example of such a change is the ejection of α and β rays during radioactive changes, for these changes are independent of temperature and volume, and therefore take place spontaneously. The liberated energy in such a case, however, becomes controllable internal energy. It would be interesting to know if the reverse may happen.

Similarly, the entropy of a substance or mixture may be divided into two parts, one of which is externally controllable while the other is not.

In speaking of the thermodynamical equilibrium of a system, such as a mixture in a number of phases, it is tacitly assumed that the nature of the equilibrium will not change unless made to do so from the outside by a change in temperature, volume, or masses of some of the constituents. The equilibrium therefore depends on the controllable internal energy and entropy of the system. Similarly, any reversible process in thermodynamics is externally controllable, and therefore involves changes only in the controllable internal energy and entropy. These particular quantities are therefore of great thermodynamical importance.

If U denote the controllable internal energy of a mass of matter, we may accordingly write

$$U = \psi_u(T,\ v,\ M_a,\ M_b, \ldots .), \quad . \quad . \quad . \quad (1)$$

where v denotes the volume of the matter at the absolute temperature T, and M_a, M_b, ... denote the masses in gram atoms of the constituents a, b, ... Similarly, if S denotes the controllable entropy, we may write

$$S = \psi_s(T,\ v,\ M_a,\ M_b, \ldots .). \quad . \quad . \quad . \quad (2)$$

Since U by definition is the controllable internal energy, it will have a zero value for certain values of v and T. For if this is not so, let U_1 denote the least possible value U can have. Now the internal energy U_1 could not be externally controlled, or its value reduced by changes in the values of v and T, and therefore it does not consist of controllable internal energy. The values of v and T corresponding to a minimum of U would therefore give a zero value to the controllable internal energy.

Similarly, it can be shown that the controllable entropy is zero corresponding to its minimum value for certain values of v and T.

If a surface is plotted with v, T, and U as axes, U being taken in its general sense, it will be evident that the zero of the controllable internal energy corresponds to a point where a plane parallel to the v and T axes touches the surface. Similarly, in the case of a surface with v, T, and S as axes, the zero of the controllable entropy corresponds to the point where a plane parallel to the v and T axes touches the surface.

The determination of the zero of these quantities depends in the main on the following theorem :—

2. *The specific heat* $\left(\frac{\partial U}{\partial T}\right)_v$ *at constant volume of a substance or mixture can have only positive values.*

This theorem is a direct consequence of our fundamental conceptions of heat and temperature, according to which an increase of temperature of a mass of matter kept at constant volume is associated with an increase in the heat content. As is well known, the thermodynamical scale of temperature is founded on Carnot's cycle. This depends on heat flowing to a substance or mixture on expanding it isothermally, and on its temperature decreasing on expanding it adiabatically. Under these conditions only can the heat taken in at the higher temperature during the cycle be larger than the heat given out at the lower temperature, the difference representing the external work done, as is demanded by the Laws of Thermodynamics. It follows also from the e laws that the

amount of work obtained is independent of the nature of the substance or mixture used, provided the operation takes place between the same temperature limits and the same amount of heat disappears as such, which forms the basis of the absolute scale of temperature. These cyclic properties may be expressed somewhat differently. Consider the well-known thermodynamical equation

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where U denotes the internal energy at the volume v, pressure p, and absolute temperature T. U may be taken to refer to the controllable internal energy because the uncontrollable part would disappear through differentiation with respect to v. Since heat flows to a substance that is expanded isothermally, $\left(\frac{\partial U}{\partial v}\right)_T + p$ is positive, and hence according to the foregoing equation $\left(\frac{\partial p}{\partial T}\right)_v$ is positive. Again, an adiabatic expansion is expressed by

$$\left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_s + p\left(\frac{\partial v}{\partial T}\right)_s = \left(\frac{\partial S}{\partial T}\right)_s = 0,$$

which becomes

$$\left(\frac{\partial U}{\partial T}\right)_v + T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_s = 0,$$

by means of equation (3). Since an adiabatic expansion is attended by a decrease in temperature $\left(\frac{\partial v}{\partial T}\right)_s$ is negative, and since we have just seen that $\left(\frac{\partial p}{\partial T}\right)_v$ is positive, it follows from the foregoing equation that $\left(\frac{\partial U}{\partial T}\right)_v$ is positive.

The foregoing reasoning will not hold if the differential coefficients $\left(\frac{\partial p}{\partial T}\right)_v$, $\left(\frac{\partial U}{\partial v}\right)_T$, $\left(\frac{\partial v}{\partial T}\right)_s$ are discontinuous, which will occur if the number and nature of the phases (and other discontinuities) changes on increasing or decreasing v or T. A more satisfactory method of reasoning is the following: Suppose that the matter has its temperature increased from T_1 to T_2 at constant volume, giving rise to an algebraical increase in entropy equal to $\sum_{T_1}^{T_2} \frac{C_v}{T} \cdot \partial T$, where

c_v denotes the specific heat at constant volume. Next suppose that the volume is adiabatically increased till the temperature has fallen to T_1, which is possible from what has gone before. Lastly, suppose that the volume of the matter is isothermally decreased till it regains its initial value. A quantity of heat Q is given out during the process according to what has gone before, and a corresponding decrease $\frac{Q}{T_1}$ in entropy takes place. This decrease is equal to the foregoing increase, and hence

$$\sum_{T_1}^{T_2} \frac{c_v}{T} \cdot \partial T = \frac{Q}{T_1}.$$

According to this equation c_v or $\left(\frac{\partial U}{\partial T}\right)_v$ is positive.

It may also be noted that since the theorem is the outcome of experience physically absurd results (in the light of our experience) will be obtained if we suppose that the theorem does not hold. Thus it is evident that if the temperature of the surrounding medium is increased by ∂T, an initial flow of heat to the substance will take place, whether its specific heat is positive or negative, otherwise nothing will ultimately happen with the substance. This would be attended by an absorption of heat. It will then be found that if we suppose that the specific heat is negative it may have an indeterminate value, or the lowering or raising of the temperature of the substance over a finite range can only be carried out by periodically reversing the flow of heat. These are, of course, absurd results in the light of our experience.

Besides the above theorem some other results will be necessary whose truth according to our experience is even more obvious, and which will therefore be designated as postulates.

3. *The coefficients* $\left(\frac{\partial p}{\partial T}\right)_v$, $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ *cannot have infinite values.*

Since the pressure of a substance is due to the motion of translation of the molecules, an increase in the magnitude of this motion through an increase of temperature is not likely to be attended by an infinite increase of pressure, or $\left(\frac{\partial p}{\partial T}\right)_v$ cannot have an infinite value. For the same reason $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ cannot have an infinite value.

We shall now proceed to apply the results of this and the preceding section.

4. *The absolute zero of the controllable internal energy of a mass of matter.*

Let us consider a mass of matter in the solid state * under the pressure of its vapour at the absolute zero of temperature. It can be shown that the controllable internal energy always increases in passing from this state to another physically possible state. Since such a change is brought about by a variation of v and T, it may be noted at the outset that the controllable internal energy only will undergo a change. Thus suppose that the matter is isothermally compressed. This can be shown to be attended by an increase in internal energy.

On multiplying the equation (3) by ∂v and integrating it between the limits v and v', U and U', we obtain

$$\mathrm{U}-\mathrm{U}'=\int_{v'}^{v}\left\{\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{v}-p\right\}\partial v.$$

At the absolute zero of temperature this equation becomes

$$\mathrm{U}-\mathrm{U}'=-\int_{v'}^{v}p\,.\,\partial v, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

since $\mathrm{T}=0$, and $\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{v}$ is not infinite according to the postulates in the preceding section. If v is taken equal to v_0, the volume of the mixture in the solid state at the absolute zero of temperature under the pressure of its vapour, and v is less than v_0, p is positive for values of v lying between v_0 and v' inclusive. Hence $\mathrm{U}'-\mathrm{U}$ is positive; or if the volume is isothermally decreased from v_0 to v', this is attended by an increase in U.

This result follows also from the fact that the atoms of a substance in the solid state at the absolute zero of temperature are in equilibrium under their forces of attraction and repulsion. Hence when the volume is decreased repulsion is the outstanding force, and the internal energy is accordingly increased during a process of compression.

Next suppose that the substance kept at the constant volume v' has its temperature increased to T. This is attended by an increase in internal energy according to the theorem of Section 2. Thus the whole process, since it involves variations of T and v, gives rise to an increase in the controllable internal energy.

Next suppose that the mass of matter in the same initial

* *I. e.* condensed state, which is likely to be that of a solid according to our experience with matter.

state as before, namely in the solid state in contact with its vapour at the absolute zero of temperature, has its volume isothermally increased to v''. The matter would divide itself into a solid and vaporous phase. The amount of matter in the latter phase would, however, be zero, since the pressure is zero. The process is therefore not attended by a change in internal energy.

Since, when v'' is infinite, the amount of evaporated matter may be finite, we may proceed more strictly thus: the heat absorbed, if any is absorbed, can only have a positive value according to the fundamental properties of Carnot's cycle pointed out in Section 2. Now the external work done is equal to ART, where A is a constant, and therefore zero, since $T=0$. Therefore a positive increase in internal energy only can take place.

Next suppose that the temperature of the matter is raised to T, keeping the volume v'' constant. This is attended by an increase in internal energy according to the theorem of Section 2. Thus the controllable internal energy of the matter has been increased during the process.

It follows, then, that the total internal energy of the mass of matter in its initial state has a smaller value than for any other physically possible state. Therefore, according to the definition of and properties of the controllable internal energy given in Section 1, its value is zero when the matter is in the solid state under the pressure of its vapour at the absolute zero of temperature.

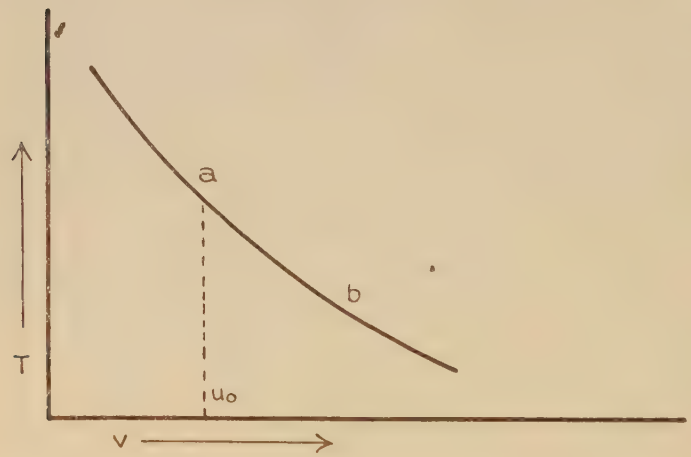
We may now proceed to the consideration of the entropy.

5. *The absolute zero of the controllable entropy of a mass of matter.*

The absolute zero of the controllable entropy according to Section 1 corresponds to the state for which it can be shown that the total entropy has a smaller positive value than for all other physically possible states. Such a state should exist. For suppose that the entropy is measured from a given state chosen arbitrarily. Let the state of greatest negative entropy be obtained corresponding to this state. We may then transfer the zero to the latter state and measure the entropy from this state. It would evidently correspond to the foregoing definition of the zero of controllable entropy.

Let the point U_0 on the v axis in the figure correspond to the zero of the controllable internal energy. Let the curve *ab* be an adiabatic corresponding to zero entropy. Now as we

pass from the zero point of internal energy U_0 to the point a on the adiabatic which corresponds to the same volume, the internal energy is increased, and hence the entropy is increased. Therefore on passing from the point a to the point U_0 the entropy is decreased; but since the adiabatic corresponds to zero entropy, the entropy should increase under these conditions. It follows, therefore, that the adiabatic must pass through U_0, or a substance or mixture in the solid state in contact with its vapour, at the absolute zero of temperature, corresponds to a state on the adiabatic of zero entropy. We may therefore take this state to correspond to zero entropy.



This zero, which is the same as that of the internal energy, will for convenience be called the absolute zero of control.

The possibility that the substance may exist in several different (crystalline) forms at the absolute zero of control which possess different internal energies and entropies remains to be considered. Suppose that two such forms are mixed at the absolute zero of temperature. The change ΔU in internal energy is given by the thermodynamical equation

$$\Delta U = T \frac{dW}{dT} - W,$$

where W denotes the external work done during the process of mixing. This may be carried out by allowing both forms to evaporate, mixing the resultant gases, and condensing the mixture. It will now be clear that the work done may be expressed in the form ΔAT, where A is a constant. Hence

when $T=0$ it follows from the above equation that $\Delta U=0$, or no change in internal energy takes place on mixing. Thus the two forms have the same internal energy, which is zero.

It can be shown that a similar result holds for the entropy. The change in internal energy during an adiabatic change is given by

$$\left(\frac{\partial U}{\partial v}\right)_s = -p,$$

which may be written

$$\left(\frac{\partial U}{\partial v}\right)_s = \left(\frac{\partial U}{\partial v}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_v$$

by means of equation (3). At the absolute zero of temperature for any state this equation becomes

$$\left(\frac{\partial U}{\partial v}\right)_s = \left(\frac{\partial U}{\partial v}\right)_T.$$

It expresses that as we pass isothermally from one form of the substance to another no change in entropy takes place.

Since this result is based on Thermodynamics, deductions made from it will not apply to substances which cannot be passed through any conceivable thermodynamical cycle. They would therefore probably not apply to such a substance as glass, which, if evaporated and condensed again, is hardly likely to be in the same state as before, *i. e.* glass. Supercooled liquids probably do not admit of being passed through a cycle, at least in some cases, and to them these restrictions will therefore also apply.

A number of relations corresponding to this zero may be found by the help of the postulates of the next section.

6. *The differential coefficients* $\left(\frac{\partial U}{\partial v}\right)_T$, $\left(\frac{\partial U}{\partial T}\right)_v$, *and* $\left(\frac{\partial S}{\partial v}\right)_T$, $\left(\frac{\partial S}{\partial T}\right)_v$ *are continuous for all possible states of a homogeneous mass of matter.*

An atom in a substance is in equilibrium under the influence of the forces of attraction and repulsion of the surrounding atoms. If these forces are not discontinuous for certain distances from their sources, the above postulates would evidently hold. There does not seem to be any evidence whatever in nature of the existence of such discontinuities.

7. Some relations at the absolute zero of control.

Since the zero of internal energy corresponds to the least value it can have, and $\left(\frac{\partial U}{\partial v}\right)_T$ and $\left(\frac{\partial U}{\partial T}\right)_v$ are not discontinuous, it follows from the Differential Calculus that the zero satisfies the conditions for a minimum, and hence we shall have:

$$\left(\frac{\partial U}{\partial v}\right)_T = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\left(\frac{\partial U}{\partial T}\right)_v = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\frac{\partial^2 U}{\partial T^2}\frac{\partial^2 U}{\partial v^2} - \left(\frac{\partial^2 U}{\partial v . \partial T}\right)^2 > 0, \quad . \quad . \quad . \quad . \quad (a)$$

$$\frac{\partial^2 U}{\partial T^2} > 0, \quad . \quad . \quad . \quad . \quad (b)$$

$$\frac{\partial^2 U}{\partial v^2} > 0, \quad . \quad . \quad . \quad . \quad (c)$$

A similar set of equations and inequalities hold for the entropy at the absolute zero of control. Since at this state the entropy has the least possible value, and $\left(\frac{\partial S}{\partial v}\right)_T$ and $\left(\frac{\partial S}{\partial T}\right)_v$ are not discontinuous according to the postulates in the preceding section, it follows that the entropy satisfies the conditions for a minimum, and hence we have:

$$\left(\frac{\partial S}{\partial v}\right)_T = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\left(\frac{\partial S}{\partial T}\right)_v = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\frac{\partial^2 S}{\partial T^2}\frac{\partial^2 S}{\partial v^2} - \left(\frac{\partial^2 S}{\partial v . \partial T}\right)^2 > 0, \quad . \quad . \quad . \quad . \quad . \quad (d)$$

$$\frac{\partial^2 S}{\partial T^2} > 0, \quad . \quad . \quad . \quad . \quad . \quad (e)$$

$$\frac{\partial^2 S}{\partial v^2} > 0. \quad . \quad . \quad . \quad . \quad . \quad (f)$$

Equation (6) expresses that the specific heat of a substance or mixture in the solid state kept at constant volume is zero at the absolute zero of temperature. This result is part of Nernst's theorem.

A formula for the specific heat of a substance in the

gaseous state at infinite volume may be found which expresses an important property of this quantity. On multiplying equation (3) by ∂v and integrating it between the limits ∞ and v, it becomes

$$U_\infty - U = \int_v^\infty \left\{ T\left(\frac{\partial p}{\partial T}\right)_v - p \right\} \partial v, \quad . \quad . \quad . \quad (9)$$

where U_∞ denotes the internal energy of the substance at infinite volume. Let us suppose that we are dealing with a mixture whose equation of state may be expanded in the form

$$p = A\frac{RT}{v} + \frac{B}{v^\alpha} + \frac{C}{v^\beta} + \ldots,$$

where A is a constant, B, C, ... functions of T, and α, β, ... positive constants whose values are greater than unity. According to our experience, this is likely to be always possible. The integral in equation (9) corresponding to the upper limit would accordingly be zero. On differentiating the equation with respect to T at constant volume, we have

$$c_v = c_{v\infty} + T\int_\infty^v \left(\frac{\partial^2 p}{\partial T^2}\right)_v \cdot \partial v, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where c_v denotes the specific heat at the volume v, and $c_{v\infty}$ that at infinite volume with the matter in the gaseous state. This equation applies to matter in any state. On applying it to a substance at the absolute zero of control the integral will not become infinite, since $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ is not infinite according to the postulates in Section 3, and the volume has the finite value v_0. The integral term therefore becomes zero, since $T=0$. Since we also have $c_v=0$, the equation gives

$$c_{v\infty} = 0; \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or the specific heat of a gas at constant infinite volume is zero at the absolute zero of temperature.

This is an interesting and important result, and is especially striking when a monatomic gas is considered. Evidence of its truth already exists. Scheele and Heuse * have measured the specific heat of helium at various temperatures and found that it decreased, though slightly, with decrease of temperature. Thus, for example, at the temperatures of 18° C. and −180° C. the specific heats were found to have the values 3·008 and 2·949 respectively.

The explanation of the result is probably that though the atom absorbs energy on increase of temperature due to an

* *Ann. der Physik*, xl. p. 484 (1913).

increase in the kinetic energy of translation, energy is also given out due to internal changes in the atom. These two changes balance each other at and near the absolute zero of temperature.

It should be mentioned that Nernst has deduced * a formula for the decrease of the specific heat of a gas with decrease of temperature from a given theory of the atomic model and quantum considerations.

Formulæ for the controllable internal energy and entropy of a substance or mixture may immediately be deduced corresponding to the volume v and absolute temperature T. Suppose that a substance or mixture at the absolute zero of control has its temperature raised to T, keeping its volume v_0 constant. The change in internal energy is equal to $\int_0^T c_{v_0} \cdot \partial T$, where c_{v_0} denotes the specific heat corresponding to the constant volume v_0. Next suppose that the volume is changed to v at constant temperature. The change in internal energy is $\int_{v_0}^{v} \partial U$. The total change in internal energy, which is the controllable internal energy U of the substance, is therefore given by

$$U = \int_0^T c_{v_0} \cdot \partial T + \int_{v_0}^{v} \partial U. \quad . \quad . \quad . \quad . \quad (12)$$

On substituting for ∂U from equation (3) and for c_{v_0} from equation (10) applied to the substance at the volume v_0, in the foregoing equation, it becomes

$$U = \int_0^T \left[c_{v\infty} + \int^{T} T \left(\frac{\partial^2 p}{\partial T^2} \right)_v \partial v \right]_{v=v_0} \partial T + \int_{v_0}^{v} \left\{ T \left(\frac{\partial p}{\partial T} \right)_v - p \right\} \partial v. \quad . \quad . \quad . \quad (13)$$

The expression for the entropy S obtained along the same lines is given by

$$S = \int_0^T \left[\frac{c_{v\infty}}{T} + \int \left(\frac{\partial^2 p}{\partial T^2} \right)_v \partial v \right]_{v=v_0} \partial T + \int_{v_0}^{v} \left(\frac{\partial p}{\partial T} \right)_v \cdot \partial v. \quad . \quad (14)$$

The value of v_0 is given by

$$v_0 = 2{\cdot}6 \, \Sigma N_w \sqrt{a_w}$$

according to Traube †, where N_w denotes the number of gram-atoms of atoms of atomic weight a_w relative to the hydrogen atom the substance contains. Thus, if the equation of state of the substance or mixture and the specific heat $c_{v\infty}$

* *Ber. d. Deuts. Phys. Gesell.* xviii. pp. 83–116 (1916).

† *Phys. Zeit.* Oct. 1909, p. 667.

be known, the controllable internal energy and entropy may immediately be evaluated. Any empirical equation of state may be used, provided its constants are determined from the facts. The controllable free energy F and the controllable thermodynamical potential Φ may then be obtained from the equations:

$$F = U - ST \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\Phi = U - ST + pv. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It will be found that in all thermodynamical formulæ useful for calculation we may substitute the controllable internal energy, entropy, free energy, and potential, since the uncontrollable parts would disappear through differentiation or otherwise.

A number of other important formulæ may be derived, which will be given in a subsequent paper.

LXXXVI. *Adsorption from the Vapour Phase at a Liquid-Vapour Interface.* *By* L. I. A. Micheli, *Ph.D.**

THE excess concentration Γ of a component at the interface between two phases may be calculated from the Gibbs equation in the form:

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\log a},$$

where a is the activity (Donnan, Rep. Brit. Ass. Adv. Soc. 1923). If the component considered be present in a vapour phase to which the laws of "perfect" gases are applicable, or in a solution so dilute as to permit the use of the laws of "ideal" solutions, the equation may be written in either of the forms:

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\log c} \quad \text{or} \quad \Gamma = -\frac{p}{RT}\frac{d\sigma}{dp}.$$

These forms of the equation have been used extensively to calculate adsorption from aqueous solutions at a water-air interface, but, in many of the cases to which they have been applied, the solutions depart so far from the "ideal" type that the use of the equations has not always been justified.

Although the case of adsorption from a vapour phase presents, from a theoretical standpoint, less serious difficulties, it has received little previous attention. Discussions have been given by Gibbs (Scientific Papers, vol. i. p. 235) and

* Communicated by Prof. F. G. Donnan, F.R.S.

by Langmuir (Journ. Am. Chem. Soc. xxxiv. p. 1898, 1917). The first systematic work, however, was carried out in this laboratory by Iredale (Phil. Mag. xlv. p. 1088, 1923 ; xlviii. p. 178, 1924 : xlix. p 603, 1925). He has determined the adsorption of a number of organic vapours at a mercury interface, and has found that the amounts adsorbed are, in every case, consistent with Langmuir's hypothesis of unimolecular layers.

Iredale has also investigated the effect of a number of organic vapours on the surface-tension of water, and has found, as a general rule, that the more soluble a substance is in water the greater is its effect on the surface-tension. His experiments also seem to indicate that the vapours of substances, even as insoluble as pentane and hexane, when they come in contact with a water surface lower appreciably its surface-tension.

The possible presence of impurities in the pentane and hexane used by Iredale renders his conclusion somewhat doubtful, so that it was proposed to investigate this phenomenon more completely. From the point of view of Langmuir's theory, this case of adsorption is of peculiar interest ; the substances are non-polar, so that a unique type of orientation might be anticipated.

It was decided to employ the "drop-weight" method for the determination of the surface-tension. The method has the advantage that measurements are always carried out with a freshly-formed surface, so that errors due to contamination are more readily avoided. This is especially important in dealing with a mercury surface.

Harkins and his co-workers (Journ. Am. Chem. Soc. xxxviii. p. 227, 1916 ; xli. p. 449, 1919 ; xlii. p. 2534, 1920) have shown that the drop-weight method can be used to give comparative results of a high degree of accuracy.

Iredale (*loc. cit.*) has also proposed a comparative method based on Worthington's equation of symmetry. For drops of similar shape

$$\frac{r_1}{r_2} = \sqrt{\frac{\sigma_1\rho_2}{\sigma_2\rho_1}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

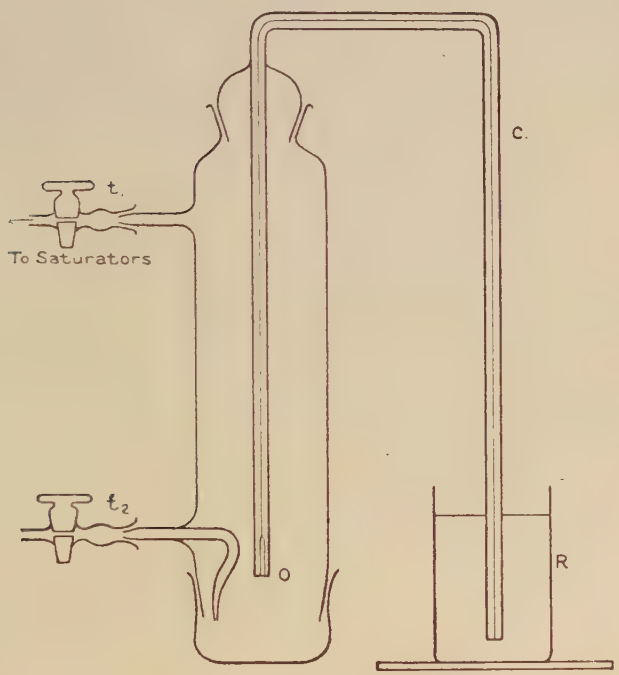
where r_1 and r_2 are the radii of the tubes from which the drops hang. In Iredale's discussion there is the implicit assumption that two drops will be similar if the ratio of the radii of the tubes from which they detach be equal to the ratio of the detached drops considered as spheres. Apart, however, from any considerations of similarity, it can be shown, quite generally, from Harkins's experimental results

that for such drops equation (1) holds good. Iredale's method of calculation has thus an experimental basis, so that the author feels justified in adopting it.

Experimental Method.

The "drop-weight" apparatus and adsorption chamber employed are represented diagramatically in fig. 1. It is

Fig. 1.



contained in an air thermostat electrically heated, and the temperature is kept constant to $\frac{1}{20}^{\circ}$ C. The liquid, whose surface-tension is being measured, is drawn from the reservoir R by means of a siphon of capillary tubing, the rate of drop formation being determined by the difference in height of the liquid in R and the orifice O, from which the drops detach. This difference in height is adjusted by means of a rack-and-pinion device operated from outside

the thermostat. When mercury is being used, it has been found necessary to have a fine constriction in the siphon of capillary tubing to reduce the rate of flow. The author has observed that, if a loosely-fitting glass rod be inserted in the end of the capillary, an equally satisfactory control is obtained and efficient cleaning of the siphon becomes possible.

The calculation of the surface-tension is based on the fact that the end of the tube from which the drops detach is circular. Methods for preparing such tubes have been described by Harkins (*loc. cit.*) and by Johlin (Journ. Phys. Chem. xxix. p. 271, 1925). The author has followed the technique described by these experimenters. Two tubes were prepared—one for mercury measurements with an accurately ground inner edge, and one for water measurements with an accurately ground outer edge. In neither case could any irregularities be detected under a magnification of about 6 diameters, and no two diameters of the same tube differed by more than 0·1 per cent.

By passing a slow stream of pure dry air through saturators filled with the liquid hydrocarbons and maintained in a water thermostat at the appropriate temperature, the adsorption chamber may be filled with a mixture of air and hydrocarbon vapour at a definite partial pressure. The following method was adopted:—When the original air in the absorption chamber has been displaced, the stream is stopped and the taps t_1 and t_2 closed. The mixture of air and vapour is now allowed to heat to the temperature of the air thermostat. The rise in temperature can be followed by the movement of liquid in the drop-weight siphon. When the temperature has become constant, the tap t_2 is opened to reduce the total pressure to atmospheric pressure and then closed once more. The partial pressure of the hydrocarbon vapour will, under these conditions, be equal to the maximum vapour-pressure at the temperature of the saturators.

The drop detachment is effected in the following manner. The reservoir R is first raised so that the drop grows very rapidly to almost its maximum size; then R is lowered so that the actual detachment takes place slowly. If water is being used, it is desirable that the whole operation be carried out as rapidly as possible to avoid errors due to evaporation. To prevent vibrations producing irregularities in the detachment, a control was devised by means of which all moving parts of the apparatus could be stopped just before the drop detaches.

It was found that, under favourable conditions, successive values of the weight of a drop differed from the mean by less than 0·1 per cent.

Origin and Purity of Materials.

NOTE.—All boiling-points are given for a pressure of 760 mm. of mercury and subject to the usual correction. Standardized thermometers were used throughout.

Benzene.—A quantity of Kahlbaum's benzene "for molecular weight determinations" was shaken with sulphuric acid for 6 hours, crystallized twice and then distilled. B.P. 80°·25 C.

Hexane.—A quantity of Kahlbaum's hexane from propyl iodide was twice fractionated, and a fraction boiling from 68°·5 C.–69°·5 C. was collected and used.

Heptane.—Several litres of commercial heptane were obtained. Small quantities of sulphur compounds and unsaturated hydrocarbons were removed by prolonged shaking with fuming sulphuric acid. Aromatic compounds were separated by nitration. After the resulting mixture had been washed repeatedly with caustic soda solution, distilled water, and finally dried, a systematic fractionation was carried out, and finally a fraction boiling between 97°·5 C.–98°·5 C. was collected and used.

Pentane and Octane.—After unsuccessful attempts to prepare a satisfactory specimen of pentane, the author was fortunate in obtaining from Prof. Sydney Young a quantity of "pure" pentane and "nearly pure" octane.

Water.—After careful investigation it was found that the water direct from the laboratory stills compared very favourably with that obtained by distillation from silica vessels, so that it was possible to use it throughout these investigations.

Mercury.—The purest available mercury was treated as follows. It was repeatedly passed through a solution of mercurous nitrate acidified with nitric acid, then twice distilled in a current of air at a pressure of 15 mm.

Adsorption at a Water-air Interface.

In the following tables is given the surface-tension of water in the presence of hydrocarbon vapours. t is the temperature of the saturators, P the partial pressure of the vapour, σ the surface-tension.

Table I.

The surface-tension of water at 25° C. in contact with benzene vapour.

t.	P (mm. Hg).	σ (dynes/cm.).
—	0	71·90
5	35·07	69·97
10	45·6	68·98
15	58·9	67·79
20	75·2	66·00
25	95·2	64·60

Table II.

The surface-tension of water at 40° C. in contact with benzene vapour.

t.	P (mm. Hg).	σ (dynes/cm.).
—	0	69·44
5	35·07	68·64
15	58·9	67·61
25	95·2	66·68
35	148·4	64·90
40	183·2	62·70

The vapour-pressures of benzene are taken from Woringer's data (*Zeit. Phys. Chem.* xxxiv. p. 257, 1900).

Table III.

The surface-tension of water at 25° C. in contact with pentane vapour.

t.	P (mm. Hg).	σ (dynes/cm.).
—	0	71·9
5	227	70·4
10	282	69·8
15	347	69·1
20	426	68·4
25	509	66·45

Table IV.

The surface-tension of water at 35° C. in contact with pentane vapour.

t.	P (mm. Hg).	σ (dynes/cm.).
—	0	70·50
5	227	69·59
10	282	69·13
15	347	68·76

TABLE V.

The surface-tension of water at 25° C. in contact with hexane vapour.

t.	P (mm. Hg).	σ (dynes/cm.).
—	0	71·9
5	59·9	71·21
10	76·81	71·01
15	97·45	70·52
20	122·5	70·33
25	152·6	69·90

TABLE VI.

The surface-tension of water at 35° C. in contact with hexane vapour.

t.	P (mm. Hg).	σ (dynes/cm.).
—	0	70·50
5	59·95	69·95
17·5	109·0	69·59
32·5	200·0	68·73
35	229·2	68·51

TABLE VII.

The surface-tension of water at 25° C. in contact with heptane vapour.

t.	P (mm. Hg).	σ (dynes/cm.).
—	0	71·9
5	15·3	71·57
10	20·4	71·32
15	27·5	71·20
20	35·5	70·88
25	46·1	70·5

TABLE VIII.

The surface-tension of water at 35° C. in contact with heptane vapour.

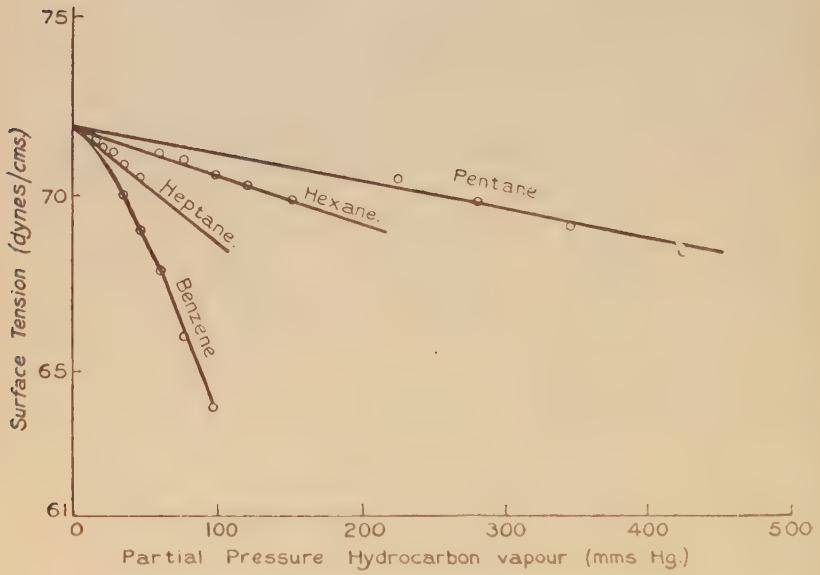
t.	P (mm. Hg).	σ (dynes/cm.).
—	0	70·5
5	15·3	70·36
10	20·4	70·24
20	35·5	70·03
30	58·5	69·74
35	73·1	69·55

The vapour-pressures of the paraffin hydrocarbons are

taken from papers of Young :—Pentane (Journ. Chem. Soc. lxxi. p. 446, 1897) ; hexane (*ibid.* lxvii. p. 1072, 1895) ; heptane (*ibid.* lxxiii. p. 675, 1898).

The data tabulated in the preceding tables are expressed graphically in figs. 2 and 3. It will be observed that in every case the $\sigma - P$ curve is a straight line, so that, along any curve, $d\sigma/dP$ is constant. The amount adsorbed for

Fig. 2



any partial pressure of the vapour can be calculated from the Gibbs equation in the form :

$$\Gamma = -C\frac{d\sigma}{dP};$$

but since $d\sigma/dP$ is constant,

$$\Gamma = K_1 C;$$

and again, since it has been assumed that the vapours conform to the laws of "perfect" gases,

$$C = K_2 P,$$

whence

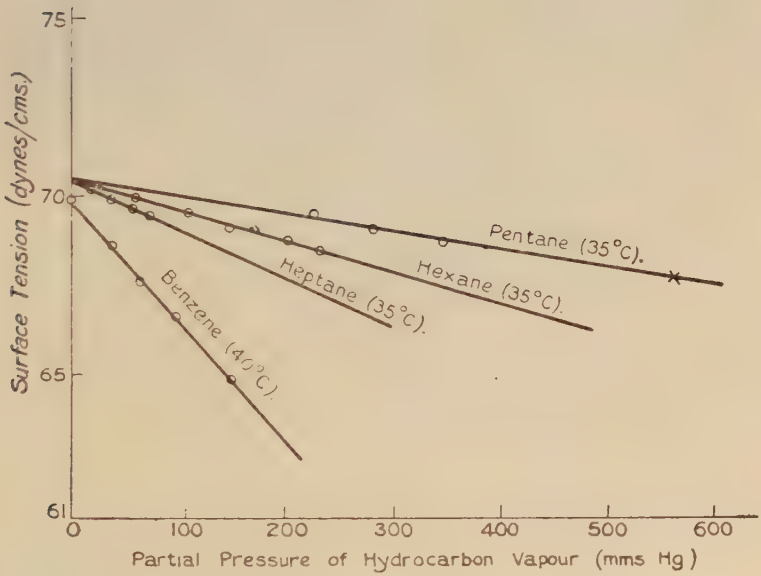
$$\Gamma = KP$$

(where K_1, K_2, and K are constants). K_1 and K, it will be

seen, depend on the particular vapour and on the temperature at which adsorption takes place.

From a knowledge of K, Γ_s, the amount adsorbed (expressed in mols per square centimetre) when the partial pressure of the vapour is equal to its maximum vapour-pressure at the temperature of adsorption, has been determined; and hence, using Millikan's value for the Avogadro number, namely $6{\cdot}06 \times 10^{23}$, a calculation has been made for S, the area per molecule adsorbed under these conditions.

Fig. 3.



These quantities for the various cases are given in Table IX.

TABLE IX.

Substance.	Temperature.	K×10⁷.	$\Gamma_s \times 10^{11}$.	S. (Å).
Benzene	25° C.	742	45·7	40·8
do.	40° C.	247	33·3	56·05
Pentane	25° C.	75	21·79	85·9 (5×17·1)
do.	35° C.	35·8	15·19	122 (5×24·4)
Hexane.....	25° C.	106	13·8	179 (6×29·9)
do.	35° C.	55·5	7·51	249 (6×41·5)
Heptane	25° C.	256	7·95	258 (7×36·9)
do.	35° C.	115	4·95	347 (7×53·7)

In a subsequent section it will be shown, from the kinetic theory of gases, that an adsorbed layer of molecules is built up very rapidly from the vapour phase ; thus, even if the vapours employed be slightly soluble, there is little possibility of the adsorbed layer being depleted by diffusion into the water so that the value of the surface tension will not be affected by the saturation of the water with the hydrocarbon.

This point was verified experimentally as follows :— Benzene was employed, as it is by far the most soluble of all the substances used. First, the surface-tension of pure water, in contact with a given partial pressure of benzene vapour, was determined, and then a similar measurement carried out, using, instead of pure water, a solution saturated with benzene vapour at this pressure. Such a solution may be formed by shaking pure water with liquid benzene at the temperature at which the chosen partial pressure is equal to the maximum vapour-pressure of benzene. The result of a series of such measurements is set out in Table X. σ is the surface-tension when pure water is employed in the dropping liquid, and σ' when the appropriate solution is used. It will be observed that σ and σ' agree within the experimental limits.

Table X.

P (mm. Hg).	σ.	σ'.
35·07	69·97	69·93
45·68	68·98	68·90
58·90	67·78	67·80
75·21	66·00	66·02

The fact that a linear relationship holds between the partial pressure of the vapour and Γ right up to the value Γ_s, and also that this quantity changes so rapidly with increasing temperature, indicate clearly that a limiting condition, such as would obtain if a closely-packed adsorbed layer were formed, had not been reached.

From column 5 in the preceding table it will be seen that the area per adsorbed molecule of pentane at 25° C. is 85·9 Å. Assuming that the molecule lies flat on the water surface, we obtain the value 17·1 Å. for each carbon atom. It is reasonable to suppose that the area occupied by closely-packed CH_2 or CH_3 groups on a water surface is not greatly different from that found by Adam at room temperature, namely 20 Å. for closely-packed OH and COOH groups ; so that, if the molecules of pentane lie flat, a closely-packed layer would be formed. This conclusion, however, is not

consistent with the form of the adsorption isotherms ; hence it seems most probable that an unsaturated unimolecular layer of molecules oriented with the CH_3 groups directed towards the water surface is formed. In the case of benzene, the values for S at 25° C. and 40° C., namely 40·8 Å and 56·05 Å respectively, are considerably greater than Adam's value, 23·8 Å (Proc. Roy. Soc. ciii. A, p. 676, 1923), for the area at room temperature occupied per molecule in a closely-packed layer of certain benzene derivatives on a water surface. In this case, clearly an unsaturated layer is formed ; and, moreover, since the phenomenon is very similar to that observed with pentane, it affords some support to the conclusion already drawn. It also seems probable that the mode of orientation of the higher member of the series is similar to that of pentane.

From the preceding table it will also be observed that, at a given temperature, K, which represents the amount adsorbed if the partial pressure of the vapour were unity and the same law held, increases rapidly as the number of carbon atoms in the paraffin molecule increases, and that, for a given substance, K decreases as the temperature rises. From the latter fact it is evident that adsorption is accompanied by an evolution of heat.

The isosteric heat of adsorption can be calculated from the Clapeyron-Clausius equation in the form :

$$H_n = RT^2 \frac{d \ln P_n}{dT},$$

where H_n is the heat of adsorption per mol at constant temperature and pressure at the stage when there are n mols adsorbed per unit area, and P_n is the corresponding partial pressure of the vapour.

If two isotherms be considered at adjacent temperatures, T_1 and T_2 respectively, and if P_1 and P_2 be the corresponding values of P_n, then taking logarithms to the base 10, as a first approximation, we may write :

$$H_n = \frac{RT_1T_2(\log P_1 - \log P_2)}{T_1 - T_2} \log_e 10.$$

Again, if k_1 and k_2 be the value of K for the particular hydrocarbon at temperatures T_1 and T_2 respectively, it follows that

$$n = K_1P_1 \text{ (at temperature } T_1)$$

$$= K_2P_2 \text{ (at temperature } T_2),$$

whence

$$(\log P_1 - \log P_2) = \log (K_2 - \log K_1);$$

so that

$$H_n = \frac{RT_1T_2(\log K_2 - \log K_1)}{T_1 - T_2}.$$

The heat of adsorption is then independent of the particular value of n, so that each equal increment in the amount adsorbed is accompanied by the same heat evolution. This is, of course, only possible when the adsorbed layer is so diffuse that the amount already adsorbed has no effect on further adsorption.

TABLE XI.

Heats of Adsorption.

Substance.	Heats of Adsorption (Kg calories).
Benzene.....	13·5
Pentane.....	13·6
Hexane	11·7
Heptane	14·6

In each case the heat of adsorption is somewhat greater than the heat of condensation at the same temperature, and seems large in comparison with many heats of adsorption recorded. However, Rideal (Journ. Chem. Soc. cxxi. p. 309, 1922), using a similar method, has obtained the value 12 Kg calories for the heat of adsorption of hydrogen on nickel, and Beebe & Taylor (Journ. Am. Chem. Soc. xxxix. p. 1892, 1917), using a direct calorimetric method, have obtained the value 13·4 Kg calories.

If the adsorbed paraffin hydrocarbon molecule lay flat on the water surface, we should expect the heat of adsorption to be roughly proportional to the number of carbon atoms in the molecule. The probable error in the heats of adsorption may amount to 20 per cent., so that the heats of adsorption of the three substances are roughly the same within the limits of accuracy. Even an accuracy of 20 per cent. is sufficient to preclude the possibility of the heats of adsorption being proportional to the number of carbon atoms in the molecule. These considerations, then, furnish some additional support for the conclusion that an end CH_3 group forms the only point of attachment to the water surface.

Adsorption at a Mercury-air Interface.

A method similar to that employed at a water-air interface was used. Some preliminary work was again carried out with benzene. Iredale (*loc. cit.*) gives values for the surface-tension of mercury in contact with a number of different partial pressures of benzene vapour at 26° C.; his values differ somewhat from the author's. The experimental results are recorded in the following tables :—

TABLE XII.

The surface-tension of mercury at 26° C. in contact with benzene vapour.

t.	P (mm. Hg).	log P.	σ (dynes/cm.).
—	0	$-\infty$	471
5	35·07	1·5449	412·0
10	45·7	1·6597	466·4
15	59·9	1·7701	398·1
20	75·2	1·8763	395·1
25	95·2	1·9784	390·9

TABLE XIII.

The surface-tension of mercury at 26° C. in contact with benzene vapour at 26° C. (Iredale).

P (mm. Hg).	log P.	σ (dynes/cm.).
0	$-\infty$	472
26·5	1·4232	415
37·0	1·5682	410
42·0	1·6232	406
49·9	1·6981	402
61·8	1·7910	400
76·3	1·8825	396
101·0	2·0043	395

TABLE XIV.

The surface-tension of mercury at 25° C. in contact with pentane vapour.

t.	P (mm. Hg).	log P.	σ (dynes/cm.).
—	0	$-\infty$	471
5	227	2·3560	413·7
10	282	2·4518	409·3
15	347	2·5403	405·4
20	426	2·6204	400·7
25	509	2·7067	392·6

TABLE XV.

The surface-tension of mercury at 25° C. in contact with hexane vapour.

t.	P (mm. Hg).	log P.	σ (dynes/cm.).
—	0	$-\infty$	471
5	59·9	1·7774	416·6
10	76·8	1·8954	413·3
15	97·45	1·9886	410·0
20	122·5	2·0881	405·7
25	152·6	2·183	403·1

TABLE XVI.

The surface-tension of mercury at 25° C. in contact with heptane vapour.

t.	P (mm. Hg).	log P.	σ (dynes/cm.).
—	0	$-\infty$	471
5	15·3	1·1847	416·2
10	20·4	1·3096	411·1
15	27·5	1·4393	407·6
20	35·5	1·5502	402·5
25	46·1	1·6637	397·9

TABLE XVII.

The surface-tension of mercury at 25° C. in contact with octane vapour.

.	P (mm. Hg).	log P.	σ (dynes/cm.).
—	0	$-\infty$	471
5	5·50	·7404	415·0
10	7·42	·8710	412·2
15	9·92	·9965	408·7
20	13·11	1·1176	403·7
25	17·13	1·2340	401·25

The surface-tension of mercury is plotted against the logarithm of the partial pressure of the hydrocarbon vapour in fig. 4. The amount adsorbed, for any concentration of the vapour, may be calculated from the Gibbs equation in the form :

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\ln C};$$

or since the validity of the "perfect" gas laws has been assumed $C = KP$, whence $d\ln C/d\sigma = d\ln P/d\sigma$, so that

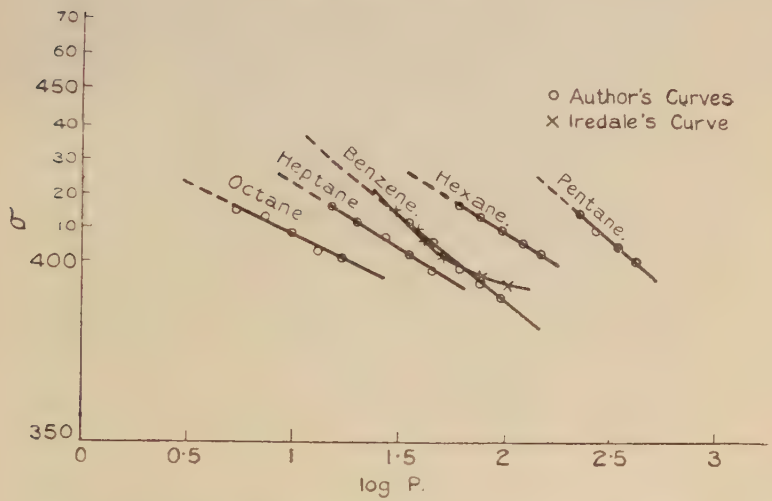
$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\ln P}.$$

That is, it is immaterial whether tangents be taken to the σ–$\ln P$ curve or to the σ–$\ln C$ curve.

In each case it will be observed that, for higher values of ln P, the curve becomes straight that is $d\sigma/d\ln P$ becomes constant, so that the amount adsorbed approaches a definite limiting value as the partial pressure of the hydrocarbon vapour increases. Iredale's σ–ln P curve for benzene vapour, however, contains a point of inflexion, and consequently the adsorption isotherm based on his data will show a maximum. Iredale appears to assume that this is the usual type of curve. It will be seen, however, that the author's curve for benzene is similar to the curves obtained

Fig. 4.

σ for a pure mercury surface = 471.



with all the paraffin hydrocarbons. It seems to the author to be, *a priori*, unlikely that the amount adsorbed should decrease as the partial pressure of the vapour increases. There are, however, several cases recorded where the adsorption isotherms based on the Gibbs equation show maxima. Rideal, for example (Proc. Roy. Soc. cix. A, p. 57, 1925), has calculated the amount of ethyl alcohol adsorbed from an aqueous solution at the liquid-air interface, and finds that there is a maximum in the adsorption isotherm whether he uses the form of the equation involving concentrations or the more accurate form involving activities. In these cases, however, it appears to the author that the observed maxima really indicate that conditions obtain which render the Gibbs equation inapplicable.

A calculation was made of Γ_s, the limiting value of Γ in

mols per square cm., and also S, the area per molecule under these conditions. The results are set out in Table XVII.

Table XVIII.

Substance.	$\Gamma_s \times 10^{11}$.	S (Å).
Benzene	80·5	20·5
Pentane	83·5	19·8
Hexane.....	71·1	23·2
Heptane	65·3	25·5
Octane	60·0	27·5

The area occupied by a benzene molecule on the mercury surface differs little from the value obtained by Adam (*loc. cit.*) for the area occupied by closely-packed molecules of certain benzene derivatives on a water surface, and also from the minimum value obtained by Iredale, though, taking the final part of his curve, where the pressure of the benzene vapour is highest, a value of 40 A is obtained.

The area per molecule found for the paraffin hydrocarbons agrees well with the values found by Adam for closely-packed molecules of straight chain aliphatic acids or alcohols oriented at a water-air interface with the OH or COOH groups attached to the surface; so that it is probable that these substances, in spite of their non-polar character, form unimolecular adsorbed layers oriented on end with the CH_3 groups behaving similarly to the polar hydroxyl and carboxyl groups. There is a gradual increase in the area per molecule as we pass from pentane to octane. This may be an effect due to the length of the "carbon chain"; but it is well to remember in drawing comparisons that the measurements are carried out over vastly different ranges of pressure. The maximum pressure of pentane available is 509 mm. of mercury, while that of octane is only 17·3 mm.

The large reduction in the surface-tension of mercury produced by contact with the vapour of substances as inactive as the paraffins is very striking. A pressure of octane vapour equal to 5 mm. of mercury lowers the surface tension 50 dynes per cm., and even at so low a pressure a closely-packed unimolecular layer is formed.

The closeness of the packing of the paraffin hydrocarbon molecules on the mercury surface enables the mode of orientation to be decided with tolerable certainty, and it is of interest to recall that at a water surface, although only unsaturated adsorbed layers are formed, evidence was obtained of a similar mode of orientation. The difference in behaviour at the two surfaces may be due in part to the difference in volatility of the two substances. From the kinetic theory of gases it follows that the mass m of a gas

at pressure p which strikes unit area of a bounding surface per second is given by

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p,$$

where M is the molecular weight.

If we consider a liquid surface in contact with its saturated vapour, since the reflectivity of vapour molecules striking the liquid surface is zero, the above equation also gives the mass which must evaporate from unit area per second. It is thus found that the time required for a number of molecules equal to that in the surface layer to evaporate is $6{\cdot}8 \times 10^{-3}$ sec. in the case of mercury and $9{\cdot}2 \times 10^{-8}$ sec. in the case of water. Again, if heptane vapour at a pressure of 15 mm. be considered, it is found that the time required for that amount, which is present in a closely-packed unimolecular layer, to strike the surface is $1{\cdot}6 \times 10^{-8}$ sec. It is thus seen that the maximum rate at which a closely-packed unimolecular layer can be formed at a water surface is comparable with the rate at which the surface is broken up by the kinetic action of its own molecules, while the mercury surface may be considered relatively permanent.

This difference in volatility must explain, in part at least, the difference between the phenomena observed in the two cases.

Summary and Conclusions.

When adsorbed from the vapour phase, at a water-air interface both benzene and the paraffin hydrocarbon vapours form unsaturated unimolecular layers. The paraffin hydrocarbon molecules are probably oriented on end: that is, with a CH_3 group directed towards the water surface. At a mercury-air interface a similar mode of orientation obtains, but closely-packed layers are formed. The difference in behaviour in the two cases is probably due in part at least to the difference in volatility of mercury and water.

Heats of adsorption at a water-air interface have been calculated, the average value being about 12 Kg calories.

My thanks are due to Prof. Sydney Young, to whom I am indebted for quantities of pure pentane and octane, and Prof. Donnan, who has suggested this investigation to me, and has given much valuable advice throughout the course of the research.

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LXXXVII. *Note on the Motion of Fluid in a Sinuous Channel.* *By* W. R. Dean, *M.A., Imperial College of Science* *.

1. In this paper the steady two-dimensional motion of incompressible fluid moving under pressure through a sinuous channel is considered. It is found necessary to assume that the channel is nearly straight, but if this assumption is made it is not necessary to suppose further that the motion is slow. The differential equation which determines the motion has been solved numerically in some typical cases; it is soluble algebraically in the case of slow motion. It is therefore possible to compare the results obtained for some given general velocity of flow with those obtained on the usual assumption of slow motion. This assumption fails to show some interesting effects, but gives a motion of the same general type and order of magnitude as the actual one; it was to be expected that the assumption would give a reasonable approximation, for the motion concerned is nearly linear, and therefore one in which the inertia terms are not of great importance.

The motion of water in a curved pipe of circular section has been studied experimentally by Prof. J. Eustice. The effect of curvature is, however, more complicated in a pipe than in a channel, for while the motion in a straight pipe is linear, that in a curved pipe is three-dimensional; it is not therefore surprising that no resemblance is found between the flow in curved pipes and curved channels. The flow of fluid over a single corrugated surface, a two-dimensional problem somewhat similar to that of this paper, has been considered by Rayleigh †, but the motion of fluid in a channel has mainly been considered as a three-dimensional problem ‡, in which form it is of great practical importance, since the currents in a river, for instance, are considerably affected by the retardation of flow by the bed.

2. If fluid is forced under pressure between parallel straight walls it is known § that (in stream-line motion) the velocity is everywhere parallel to the walls, and that rate of flow and pressure gradient are connected by the equation

$$\int_{-h}^{h} u\,dz = -\frac{2h^3}{3\mu}\frac{\partial p}{\partial x}, \qquad \ldots\ldots (1)$$

* Communicated by Prof. S. Chapman, F.R.S.

† 'Collected Papers,' iv. p. 78.

‡ Osborne Reynolds, 'Scientific Papers,' ii. pp. 326, 380; James Thomson, Roy. Soc. Proc. A, xxv. p. 5 and xxvi. p. 356.

§ H. Lamb, 'Hydrodynamics' (4th edition), § 330.

where u is the velocity in the direction of the x axis at a point whose perpendicular distance from the central plane is z, $z=\pm h$ are the walls, p is the pressure, and μ the coefficient of viscosity.

It is known further that these results are only slightly modified if the walls of the channel are concentric circular cylinders ; for comparison with what follows the equations for this problem are written down. The equations of motion, referred to polar coordinates (r, θ), for steady two-dimensional motion are

$$u\frac{\partial u}{\partial r}+\frac{v}{r}\frac{\partial u}{\partial \theta}-\frac{v^2}{r}=-\frac{\partial}{\partial r}\left(\frac{p}{\rho}\right)+\nu\left(\nabla_1^2 u-\frac{u}{r^2}-\frac{2}{r^2}\frac{\partial v}{\partial \theta}\right),$$

and

$$u\frac{\partial v}{\partial r}+\frac{v}{r}\frac{\partial v}{\partial \theta}+\frac{uv}{r}=-\frac{1}{r}\frac{\partial}{\partial \theta}\left(\frac{p}{\rho}\right)+\nu\left(\nabla_1^2 v-\frac{v}{r^2}+\frac{2}{r^2}\frac{\partial u}{\partial \theta}\right),$$

while the equation of continuity is

$$\frac{\partial u}{\partial r}+\frac{u}{r}+\frac{1}{r}\frac{\partial v}{\partial \theta}=0.$$

Assuming that $u=0$, and that v is independent of θ, the equation of continuity is satisfied, and the first two equations become

$$-\frac{v^2}{r}=-\frac{\partial}{\partial r}\left(\frac{p}{\rho}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$0=-\frac{1}{r}\frac{\partial}{\partial \theta}\left(\frac{p}{\rho}\right)+\nu\left(\frac{d^2 v}{dr^2}+\frac{1}{r}\frac{dv}{dr}-\frac{v}{r^2}\right) \quad . \quad . \quad (3)$$

Let $$p/\rho=k\theta+f(r),$$

where k is constant ; then v must satisfy the equation

$$\frac{d^2 v}{dr^2}+\frac{1}{r}\frac{dv}{dr}-\frac{v}{r^2}=\frac{k}{\nu r},$$

and must therefore be given by

$$v=\mathrm{A}/r+\mathrm{B}r+kr\log r/2\nu.$$

From the boundary condition that $v=0$ when $r=a\pm h$, A and B can be found, while $f(r)$, which determines the variation in pressure across a section of the channel, is given by (2). There is not as in the previous case a constant pressure gradient, but regarding G $(=k\rho/a)$ as the mean

pressure gradient, we have the relation

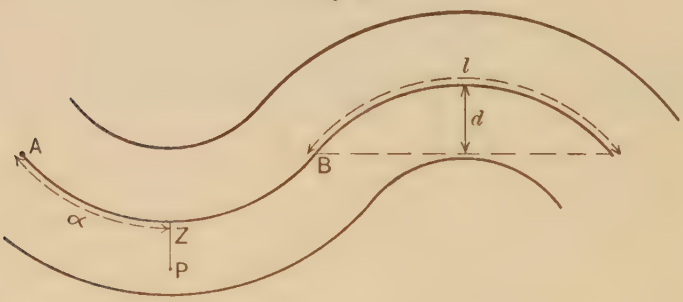
$$\int_{a-h}^{a+h} v\,dr = \frac{G}{8\mu h}\left[(a^2-h^2)^2\left\{\log\frac{a+h}{a-h}\right\}^2 - 4a^2h^2\right], \quad (4)$$

which corresponds to (1) and reduces to it when h/a is small. It can be verified from (4), and is clear physically, that to produce a given rate of flow a larger pressure gradient is required in a curved channel than in a straight one.

The only other consequence of the curvature is that the pressure varies across the section of the channel. The curvature does not cause a departure of the stream-lines from parallelism with the walls ; for this effect we must turn to a different problem.

3. We now consider the two-dimensional motion of fluid forced under pressure through a sinuous channel. The following coordinates (α, z) can conveniently be used. From any point P draw PP_0 normal to the line midway between the walls, and let its length be z. Let the distance of P_0

Fig. 1.



measured along the central line from a fixed point (A in fig. 1) be α. Let U, V be the orthogonal components (corresponding to the coordinates α, z) of the velocity at P.

The curvature of the central line, c, is assumed given by

$$c = k\sin n\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where k and n are constants, k being the maximum curvature. The walls of the channel are the surfaces $z = \pm h$.

Referred to these coordinates the equations of steady motion are

$$\frac{U}{1+cz}\frac{\partial U}{\partial\alpha} + V\frac{\partial U}{\partial z} + \frac{cUV}{1+cz} = -\frac{1}{1+cz}\frac{\partial}{\partial\alpha}\left(\frac{P}{\rho}\right)$$
$$-\nu\frac{\partial}{\partial z}\left[\frac{1}{1+cz}\left\{\frac{\partial V}{\partial\alpha} - (1+cz)\frac{\partial U}{\partial z} - cU\right\}\right],$$

and

$$\frac{U}{1+cz}\frac{\partial V}{\partial \alpha}+V\frac{\partial V}{\partial z}-\frac{cU^2}{1+cz}=-\frac{\partial}{\partial z}\left(\frac{P}{\rho}\right)$$
$$+\frac{\nu}{1+cz}\frac{\partial}{\partial \alpha}\left[\frac{1}{1+cz}\left\{\frac{\partial V}{\partial \alpha}-(1+cz)\frac{\partial U}{\partial z}-cU\right\}\right],$$

where P is the pressure. The equation of continuity is

$$\frac{1}{1+cz}\left[\frac{\partial U}{\partial \alpha}+\frac{\partial}{\partial z}\left\{(1+cz)V\right\}\right]=0.$$

These equations reduce to Cartesian equations for two-dimensional motion if $c=0$, and to equations in cylindrical coordinates if c is treated as a constant, and r substituted for $(1+cz)/c$.

4. It has not been found possible to make progress with the equations as they stand, so we now introduce the assumption that the curvature of the channel is small. If the channel were straight we should have $c=0$, and the equations could be satisfied by

$$U=A(h^2-z^2),\ V=0,\ P/\rho=-2\nu A\alpha,$$

A being constant; in a slightly curved channel the motion and pressure variation approximate to those of this simple case. We therefore write

$$U=A(h^2-z^2)+u,\ V=v,\ P/\rho=-2\nu A\alpha+p/\rho\ ;$$

we then neglect the second powers and products of u and v, and the first powers of these variables (and of p) if multiplied by some such function as cz. The three equations then become

$$A(h^2-z^2)\frac{\partial u}{\partial \alpha}+v(-2Az)=-\frac{\partial}{\partial \alpha}\left(\frac{p}{\rho}\right)$$
$$-4\nu Acz+\nu\left(\frac{\partial^2 u}{\partial z^2}-\frac{\partial^2 v}{\partial \alpha\partial z}\right),\quad (6)$$

$$A(h^2-z^2)\frac{\partial v}{\partial \alpha}-cA^2(h^2-z^2)^2=-\frac{\partial}{\partial z}\left(\frac{p}{\rho}\right)$$
$$-\nu A(h^2-z^2)\frac{\partial c}{\partial \alpha}+\nu\left(\frac{\partial^2 v}{\partial \alpha^2}-\frac{\partial^2 u}{\partial z\partial \alpha}\right),\quad (7)$$

and

$$\frac{\partial u}{\partial \alpha}+\frac{\partial v}{\partial z}=0\quad .\ .\ .\ .\ .\ .\ .\quad (8)$$

These equations are soluble and provide a first approximation to the problem considered.

5. Inserting the value of c, and writing

$$u = u_1 \cos n\alpha + u_2 \sin n\alpha,$$
$$v = v_1 \cos n\alpha + v_2 \sin n\alpha,$$
$$p = p_1 \cos n\alpha + p_2 \sin n\alpha,$$

we find that the equations (6), (7), and (8) can be satisfied if six relations connect the quantities u_1, u_2, v_1, ..., which are functions of z only. The six relations can be combined in pairs to form three equations in the complex functions u', v', and p' which are respectively equal to $u_1 + iu_2$, $v_1 + iv_2$, and $p_1 + ip_2$. The equations are

$$-i\mathrm{A}(h^2-z^2)nu' - 2\mathrm{A}zv' = inp' - 4i\mathrm{A}\nu kz + \nu\left(\frac{d^2u'}{dz^2} + in\frac{dv'}{dz}\right), \quad . \quad . \quad . \quad (9)$$

$$-i\mathrm{A}(h^2-z^2)nv' - i\mathrm{A}^2(h^2-z^2)^2k = -\frac{dp'}{dz} - \nu\mathrm{A}(h^2-z^2)kn + i\nu n\left(\frac{du'}{dz} + inv'\right), \quad . \quad (10)$$

and

$$\frac{dv'}{dz} = inu'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If p' and u' are eliminated it is found that v' must satisfy the equation

$$\nu\left(\frac{d^4v'}{dz^4} - 2n^2\frac{d^2v'}{dz^2} + n^4v'\right) + i\mathrm{A}n\left\{(h^2-z^2)\left(\frac{d^2v'}{dz^2} - n^2v'\right) + 2v'\right\} = -4\mathrm{A}\nu kn + i\mathrm{A}^2(h^2-z^2)^2kn^2 - \nu\mathrm{A}(h^2-z^2)kn^3. \quad . \quad . \quad (12)$$

When v' is known u' can be determined from (11).

The equation (12) can be put in non-dimensional form by the substitutions

$$z' = z/h, \qquad v' = \mathrm{A}h^2v'';$$

we then have

$$\left(\frac{d^4v''}{dz'^4} - 2n^2h^2\frac{d^2v''}{dz'^2} + n^4h^4v''\right) + \frac{i\mathrm{A}nh^4}{\nu}\left\{(1-z'^2)\frac{d^2v''}{dz'^2} + 2v''\right\} - \frac{i\mathrm{A}n^3h^6}{\nu}(1-z'^2)v'' = -4knh^2 - kn^3h^4(1-z'^2) + \frac{i\mathrm{A}kn^2h^6}{\nu}(1-z'^2). \quad . \quad (13)$$

At the walls, $z = \pm h$, the velocity of the fluid must vanish ; the conditions for this in terms of v'' and z' are

$$v'' = \frac{dv''}{dz'} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

when $z' = \pm 1$.

6. When the constants in equation (13) are known, the numerical solution (no other appears possible) is straightforward. Writing

$$v'' = A_0 + A_2 z'^2 + A_4 z'^4 + \ldots ., \quad . \quad . \quad . \quad (15)$$

where the A's are constants, and substituting in (13), we have a series of relations from which A_4, A_6, ... can successively be found in terms of A_0, A_2 and the constants of the equation.

The conditions (14) require

$$A_0 + A_2 + A_4 + \ldots . = 0, \quad . \quad . \quad . \quad . \quad (16)$$

and

$$A_2 + 2A_4 + 3A_6 + \ldots . = 0. \quad . \quad . \quad . \quad . \quad (17)$$

Substituting in these equations the values of A_4, A_6, ..., we have two equations from which A_0 and A_2 can be determined.

7. There does not appear to be an accepted experimental value for the critical velocity of fluid flowing under pressure between parallel straight walls. Orr's theoretical result * is $d\bar{u}/\nu = 117$, where d is the distance between the walls, and $\bar{u}$ the mean velocity across a section. Higher values have, however, been obtained theoretically †, and there is a higher experimental value ‡, about 300, for the more unstable condition of flow in an open stream. If $u = A(h^2 - z^2)$, according to Orr's result the critical value of the non-dimensional constant Ah^3/ν is 87·75 ; but this value is possibly too low. However, it is known § that curvature in a pipe conveying fluid causes a very large reduction in the critical velocity, and it may be assumed that the effect of a curvature in a channel is the same. No value of Ah^3/ν greater than 100 has therefore been considered in the numerical work.

The constant n is equal to π/l if l is the length of a bay of the central line ; the assumption of small curvature requires that h/l, and therefore nh, shall be small. The value of nh

* Proc. Roy. Irish Acad. vol. xxvii. p. 76.

† For instance, Osborne Reynolds, 'Scientific Papers,' vol. ii. p. 575, gave the value 517 and considered a higher experimental value probable.

‡ Hopf, *Ann. der Phys.* vol. xxxii. (1910).

§ Gibson and Grindley, Proc. Roy. Soc., A, vol. lxxx.

has generally been taken as 0·1, the corresponding ratio of length of bay to semi-width of channel being 31·4, but in the case $A/h^3\nu = 100$ numerical work has been done with the two further values 0·2 and 0·3 of nh.

The constant k has been assumed equal to hn^2, and this is roughly to assume that d, the depth of a bay of the central line, is equal to h. For

$$d = \int_0^{\pi/2n} \sin\left(\frac{k}{n}\cos n\alpha\right) d\alpha,$$

$$= \frac{k}{n^2}\left[1 - \frac{2}{3.3\,!}\left(\frac{k}{n}\right)^2 + \frac{2.4}{3.5.5\,!}\left(\frac{k}{n}\right)^4 - \ldots\right]; \quad . \quad (18)$$

if $k = hn^2$ the depth of bay is given by

$$d/h = 1 - \frac{2}{3.3\,!}n^2h^2 + \ldots,$$

so that d and h differ by less than 1 per cent. when nh has its largest value 0·3. In view of the other approximations this accuracy is more than sufficient, and the results may be taken as referring to the case $d = h$. They can, however, be applied immediately to different cases, since v' is directly proportional to k. Thus twice the value of v' obtained in any case gives the velocity when $k = 2hn^2$; the corresponding value of d, which will be approximately $2h$, can be found from (18) for the known value of nh.

8. A sufficient knowledge of the motion of the fluid as a whole can be gained if the velocity at all points of the central line is found. At any such point $z' = 0$, and we have from (11) and (15)

$$v' = A_0, \quad u' = 0;$$

hence it is only necessary to find A_0.

The convergence of the series in (16) and (17) is fairly rapid. When $A/h^3\nu = 50$ it is only necessary to calculate the coefficients up to and including A_{12}; substituting in (16) and (17), we have

$$(-1389 + 2045\,i)10^{-7} + A_0(\cdot 9434 - \cdot 4111\,i) + A_2(\cdot 9447 - \cdot 4132\,i) = 0,$$

and

$$(-2561 + 4024\,i)10^{-7} + A_0(-\cdot 1574 - \cdot 8168\,i) + A_2(\cdot 8448 - \cdot 8209\,i) = 0,$$

whence

$$A_0 = (-1894 + 1274\,i)10^{-7}.$$

We can then write this

$$A_0 = (-1\cdot 89 + 1\cdot 27\,i)10^{-4}. \quad . \quad . \quad . \quad (19$$

When $Ah^3/\nu=75$ the corresponding value is given by

$$A_0=(-2{\cdot}14+1{\cdot}83\,i)10^{-4}, \quad . \ . \ . \quad (20)$$

and when $Ah^3/\nu=100$, by

$$A_0=(-2{\cdot}45+2{\cdot}31\,i)10^{-4}. \quad . \ . \ . \quad (21)$$

The results of (19), (20), and (21) all refer to the case $nh=0{\cdot}1$ and $k=hn^2$, in which the length of bay is $31{\cdot}4\,h$ and its depth approximately h.

When $Ah^3/\nu=100$ two further values of nh, $0{\cdot}2$ and $0{\cdot}3$, have been used (with the same expression for k) to find the effect of a smaller ratio of l/h; that is, of a more rapid corrugation of the channel.

When $nh=0{\cdot}2$, or $l/h=15{\cdot}7$,

$$A_0=(-3{\cdot}01+2{\cdot}73\,i)10^{-3}, \quad . \ . \ . \quad (22)$$

while when $nh=0{\cdot}3$, or $l/h=10{\cdot}5$,

$$A_0=(-1{\cdot}27+1{\cdot}03\,i)10^{-2}. \quad . \ . \ . \quad (23)$$

In the last case the calculation is the longest; it is then necessary to find the coefficients up to A_{24}.

9. To these results we may add that obtained on the assumption that the motion is slow. The terms on the left-hand sides of equations (6) and (7) then disappear, and in place of (12) we have the equation

$$\nu\left(\frac{d^4v'}{dz^4}-2n^2\frac{d^2v'}{dz^2}+n^4v'\right)=-4A\nu kn-\nu A(h^2-z^2)kn^3,$$

and hence in place of (13),

$$\frac{d^4v''}{dz'^4}-2n^2h^2\frac{d^2v''}{dz'^2}+n^4h^4v''=-4knh^2-kn^3h^4(1-z'^2).$$

Since nh is small, a further approximation * can be made, and the last equation reduced to

$$\frac{d^4v''}{dz'^4}=-4knh^2.$$

The solution of this that satisfies the boundary conditions (14) is

$$v''=-\frac{knh^2}{6}(1-2z'^2+z'^4),$$

so that denoting as above the value of v'' when $z'=0$ by A_0, we have

$$A_0=-knh^2/6. \quad . \ . \ . \ . \ . \quad (24)$$

* This approximation has not actually been made in the treatment of the full equation (13), as it would lead merely to slightly different constants in the equation and effect hardly any simplification in the numerical work.

10. It has been remarked that at any point of the central line u', and therefore u, vanishes, so that at all such points the velocity of the fluid in the direction of the channel is the same, Ah^2. The normal component of the velocity at any point of the channel is

$$v_1 \cos n\alpha + v_2 \sin n\alpha,$$

where v_1 and v_2 are the real and imaginary parts of Ah^2v''. We know in the cases considered the values of v'' when $z'=0$, and hence the magnitude and direction of the velocity at all points of the central line, but without further calculation the stream-lines in the centre of the channel can be found with sufficient accuracy. The differential equation to a stream-line is

$$\frac{1}{1+cz}\frac{dz}{d\alpha} = V/U,$$

U and V being functions of α and z. It has been seen that V is small in comparison with U; hence a stream-line that passes through a point of the central line will not deviate far from the centre in the neighbourhood of the point concerned. Approximately, the differential equation to this portion of the stream-line is therefore

$$\frac{dz}{d\alpha} = \{(v_1)_0 \cos n\alpha + (v_2)_0 \sin n\alpha\}/Ah^2, \quad . \quad . \quad (25)$$

where $(v_1)_0$ and $(v_2)_0$ are the values of v_1 and v_2 when $z'=0$. The coefficients of $\cos n\alpha$ and $\sin n\alpha$ in (25) are clearly the real and imaginary parts of A_0.

We may express this approximate result by saying that the central stream-lines are sine curves, by which is meant curves such that the departure of any point from the central line is a circular function of the distance of the point along the channel. The motion thus indicated does not contradict the assumption made in deriving it. If the approximation were to show a progressive departure of the stream-lines from the centre, it would be clear that the approximation could only be valid in a limited region; the contrary being the case, the result may be assumed of sufficient accuracy.

11. Fig. 2, which is not drawn to scale, shows the form of the stream-lines in two different cases. Consider first slow motion through a channel such that $nh=0{\cdot}3$ and $k=hn^2$, that is, such that $l/h=10{\cdot}5$ and $d/h=1$. From (24)

$$A_0 = -4{\cdot}5 \times 10^{-3};$$

the approximate differential equation to a central stream-line is therefore

$$\frac{dz}{d\alpha} = -(4{\cdot}5 \times 10^{-3}) \cos n\alpha,$$

and for the stream-line through the point A we get a curve of the type shown by the dotted line in fig. 2. If the flow of fluid through the same channel is such that $Ah^3/\nu = 100$, the value of A_0 is given by (23), and the approximate differential equation is

$$\frac{dz}{d\alpha} = -(1{\cdot}64 \times 10^{-2}) \cos (n\alpha + {\cdot}68).$$

The stream-line through A is of the form shown by the chain-dotted line in fig. 2. The full line represents the central line of the channel; the walls are not shown.

Fig. 2.

In slow motion the slight departure that actually takes place from a motion following the lines of the channel is evidently such that the stream-lines are straightened. This is also the case when the motion is more rapid; for the curvature of a central stream-line is approximately $k \sin n\alpha - \frac{d^2z}{d\alpha^2}$, and thus of the form $k \sin n\alpha - a \sin (n\alpha + \theta)$, where a is a positive constant. The maximum of this expression is less than k if, as is the case here, a/k is small and θ less than $\pi/2$.

It is interesting to compare the results of equations (19) to (23) with those obtained on the assumption of slow motion. The comparison for one case has just been given. The inclination of a central stream-line to the line of the channel is more than three times that indicated by the assumption of slow motion, but is of the same order of magnitude. The error of the assumption is greatest in this

case. When $Ah^3/\nu = 100$ and $nh = 0{\cdot}2$, the value of A_0 given by (22), $(-3{\cdot}01 + 2{\cdot}73\,i)10^{-3}$, is to be compared with $-1{\cdot}33 \times 10^{-3}$ given by (24). When $nh = 0{\cdot}1$ we have three values of A_0, $(-1{\cdot}89 + 1{\cdot}27\,i)10^{-4}$, $(-2{\cdot}14 + 1{\cdot}83\,i)10^{-4}$, and $(-2{\cdot}45 + 2{\cdot}31\,i)10^{-4}$, corresponding to the values 50, 75, and 100 of Ah^3/ν. The assumption of slow motion leads to a value of A_0 that does not depend on the velocity, and therefore indicates that the shape of the stream-lines does not depend on the velocity. The three values of A_0 above have therefore to be compared with the single value $-1{\cdot}67 \times 10^{-4}$ from (22).

For the problem considered a reasonable approximation is obtained if the assumption of slow motion is made. This is not surprising; for the motion is nearly linear, and if it were exactly so the inertia terms would vanish.

12. The stream-line motion of water in curved pipes of circular cross section has been studied experimentally by Prof. J. Eustice *. There is, however, little resemblance between this problem and the one considered here. In each case, of course, the flow caused by a given pressure gradient is reduced as the result of curvature, but the two types of motion are quite different. Thus one of the results established experimentally is that if the velocity of flow in a curved pipe is increased, the departure of the stream-lines from the central line of the pipe is decreased. We have seen that the reverse is true in flow in a curved channel.

The general explanation of the motion of fluid in a pipe given in the paper quoted † makes it clear that the difference is not remarkable. This explanation is roughly as follows: consider a pipe of circular section in the form of a U-tube, in which fluid flows along one of the straight arms and into the bend. An element of the fluid that in the straight part of the tube is moving along the central line has, when it reaches the bend, a tendency to continue in a straight line. It therefore exerts pressure on the fluid in the outer part of the bend, and the latter is forced from the central plane (a plane through the axes of the straight parts of the tube) round the walls to the inner curve, part going above the central plane and part below. The motion of this part of the fluid is somewhat like that of a jet which spreads when it strikes a surface inclined to its direction. The observed motion of the water can be accounted for in this way. If now the velocity of flow is increased the fluid element considered has a stronger tendency to go straight to the

* Proc. Roy. Soc., A, vol. lxxxv. p. 119.
† *Loc. cit.* p. 127.

outer wall, but more pressure is required to force the outer fluid round the wall to the inner curve. The second effect must be the more important, for the experimental result is that with increased velocity the fluid element reaches the outer curve at increased distance from the beginning of the bend.

This explanation rests entirely on the fact that in a pipe three-dimensional motion is possible, and therefore does not apply to the more restricted motion in a channel that has been considered here.

13. Fig. 2 shows how stream-lines in a channel vary in shape with the velocity of flow. Of this there appears to be no obvious explanation, but the result obtained can be accounted for to some extent as follows. Let us consider what external forces are necessary to maintain in a sinuous channel a motion of exactly the same type as that which actually takes place in a straight channel, under the same conditions as to pressure; that is to say, to maintain the motion

$$U = A(h^2 - z^2), \quad V = 0, \qquad . \quad . \quad . \quad . \quad (26)$$

given that $P/\rho = -2\nu A\alpha$.

From (6) and (7) we must have a force in the direction of the channel of amount $4\mu Acz$, or $-2\mu c dU/dz$, while in the perpendicular direction the force must be

$$\mu U \frac{dc}{d\alpha} - \rho c U^2. \qquad . \quad . \quad . \quad . \quad . \quad (27)$$

The terms in μ represent forces required to overcome the resistances to the additional distortion that takes place in this motion as compared with the corresponding motion in a straight channel, while the other term represents the force required to balance the kinetic reaction of the moving fluid. In the absence of these applied forces there is a probability that the alteration in motion at any point will be in the direction opposite to the force required at this point to maintain the motion (26). This is no more than a rough approximation, for the altered pressure distribution in the actual motion modifies to an unknown extent the simple effect of the unbalanced forces. If, for instance, the applied forces can be derived from the pressure alteration (that is, in effect, from a potential) the motion does actually take place along the lines of the channel * ; but this evidently does not

* Practically this is the case in flow in a circular channel, § 2.

happen here, and it is in fact possible to explain as suggested the different shapes of the stream-lines according as the velocity is high or low.

In effect we are concerned only with the applied force perpendicular to the direction of the channel; the component along the channel is evidently of minor importance in determining the configuration of the stream-lines. In slow motion the term $-\rho c U^2$ in (27) can be neglected in comparison with the other; the force to be applied at any point of the central line is therefore $\mu A h^2 k n \cos n\alpha$, which is of maximum intensity at such points as A and B (fig. 2), is in the direction of $z+^{ve}$ at A, and the reverse at B. According to our assumption the actual motion can be regarded as disturbed from flow along the line of the channel by forces opposite in direction to the above, and this assumption is clearly sufficient to explain the form of the stream-lines in slow motion.

If the motion is not slow the applied force at any point of the central line is

$$\mu A h k \left\{ nh \cos n\alpha - \frac{A h^3}{\nu} \sin n\alpha \right\},$$

the second term being the more important except near A and B, at which points it vanishes. The force corresponding to the second term is of maximum intensity at C and D, being at these points in the directions of $z-^{ve}$ and $z+^{ve}$ respectively. Again in this case by supposing that forces opposite in direction act we can roughly account for the form of the stream-lines.

Finally, the applied force system is proportional to the velocity in slow motion, while in rapid motion the more important force is proportional to the square of the velocity; we have therefore a tentative explanation of the results that have been found that in rapid motion the stream-lines are more inclined to the line of the channel than in slow motion, and that in slow motion (but only in this case) the shape of the stream-lines is independent of the velocity.

LXXXVIII. *On the Application of Kinetic Theory to Surface Films.* *By* Kshitish Chandra Sen, *D.Sc.*, *Department of Chemistry, Allahabad University, India* *.

In the second part of his well-known paper on the Fundamental Properties of Solids and Liquids, Langmuir (Journ. Amer. Chem. Soc. 1917, xxxix. p. 1858) has shown how it is possible to draw an analogy between a surface film on a liquid and the behaviour of a gas so far as the relation $p.v=R.T$ is concerned. It was previously suggested by Devaux (Ann. Report Smithsonian Inst. 1913, p. 261) that a film on a liquid surface may exist in the three states of matter—namely solid, liquid, and gas; and it has been shown by Schofield and Rideal (Proc. Roy. Soc. 1925, cix. p. 57; 1926, cx. p. 167) that the film in the gaseous state obeys a law connecting the area and surface pressure of the molecules which is practically of the same form as $p.v=R.T$ for gases. Just as the simple gas law breaks down in the region of high pressure and the value of pv/RT no longer remains unity, so also the value of the ratio FA/RT—where F is the surface pressure of the molecules and given by the relation $F=\sigma_0-\sigma$, where σ_0 is the original surface tension of pure liquid and σ is the surface tension of the liquid when the film is formed, and A is the area occupied by one gram mole of the substance comprising the film—shows also considerable variation with the increase in the value of F. In other words, with higher values of F the deviation from the ratio FA/RT is of the same nature as that shown by gases under high compression. It has been shown by Amagat that the pv/RT—p curves for gases under high compression approximate to straight lines, and thus can be represented by an equation of the type

$$\frac{pv}{RT}=\frac{b}{RT}\cdot p+x,$$

where b is the volume occupied by a mole of the gas under high compression, and $1/x$ gives a measure of the lateral cohesion of the molecules. Recently Schofield and Rideal (*loc. cit.*) have applied an equation of a similar form to represent the behaviour of surface films, which is written as follows:

$$\frac{FA}{RT}=\frac{B}{RT}\cdot F+x.$$

* Communicated by Prof. Meghnad Saha.

This equation fairly satisfactorily represents the data of several experimental results, such as some of the fatty acids in water, butyric acid in benzene-water interface, etc. The object of the present article is to study some more experiments in relation to this equation of state, the systems chosen being dimethylaniline films in benzene-water and heptane-water interfaces.

Method of Evaluation of FA/RT *in the case of Surface Films.*

When a dissolved substance decreases the surface tension of water, the excess concentration in the surface is given by Gibbs' law,

$$\Gamma = -\frac{C}{RT}\cdot\frac{d\sigma}{dC} = -\frac{d\sigma}{2{\cdot}303RTd\log_{10}C},$$

where C is the molar concentration. Under these conditions, Γ is expressed in moles per sq. cm., and hence $A = \frac{1}{\Gamma}$, where A is the area occupied by one mole in the surface film.

Hence

$$A = -\frac{2{\cdot}303\,RTd\log_{10}C}{d\sigma}.$$

Also, by definition,

$$F = \sigma_0 - \sigma\ ;$$

$$\therefore\quad d\sigma = -dF$$

(assuming σ_0 to remain constant).

Hence

$$A = \frac{2{\cdot}303\,RTd\log_{10}C}{dF}\ ;$$

$$\therefore\quad \frac{FA}{RT} = \frac{2{\cdot}303d\log_{10}C}{dF}\ .\ F.$$

If S denotes the slope of the curve $F - \log_{10}C$, then

$$\frac{FA}{RT} = 2{\cdot}303\frac{F}{S}.$$

The value of $\frac{FA}{RT}$ has been evaluated by the use of this equation.

Experimental Results and Discussion.

The effect of dimethylaniline on the interfacial tension between benzene and water and heptane and water has been determined by Mathews and Stamm (Journ. Amer. Chem.

Soc. 1924, xlvi. pp. 1071, 2880). Columns 1 and 2 of Tables I. and III. are taken from their data. S is obtained

TABLE I.

Heptane-Water Interface.

1. P.c. dimethylaniline by vol.	2. Surface tension.	3. F.	4. $\log_{10}$ C (C=mole/litre).
0	50·39	—	—
1·19	46·48	3·91	$\bar{2}$·9734
7·14	39·65	10·74	1·7516
14·3	36·22	14·17	0·0532
25·0	33·49	16·7	0·2958
50·0	30·98	19·41	0·5968
75·0	28·23	22·16	0·7729

TABLE II.

Heptane-Water Interface.

F.	S.	$2{\cdot}303\frac{F}{S}=\frac{FA}{RT}$.
5	8·08	1·42
8	9·32	1·97
10	9·75	2·35
15	11·08	3·10
18	11·66	3·55

TABLE III.

Benzene-Water Interface.

1. P.c. dimethylaniline by vol.	2. Surface tension.	3. F.	4. $\log_{10}$ C (C=mole/litre).
0	34·71	—	—
3·0	33·93	0·78	$\bar{1}$·3750
6·22	33·33	1·34	$\bar{1}$·6917
7·14	33·25	1·46	$\bar{1}$·7516
11·10	32·45	2·26	$\bar{1}$·9432
13·90	32·12	2·59	0·0409
16·70	31·50	3·21	0·1206
22·70	31·15	3·56	0·2539
33·33	30·4	4·31	0·4207
50·00	28·98	5·73	0·5969
57·20	28·68	6·03	0·6553
71·50	27·65	7·06	0·7522
83·30	26·78	7·93	0·8185

by plotting F against $\log_{10}$ C, drawing the best curve through the points and drawing the tangents at particular values of F. In Tables II. and IV. the calculated values of FA/RT for particular values of F are shown. In calculating the concentration of dimethylaniline, the density has been taken to be 0·9565.

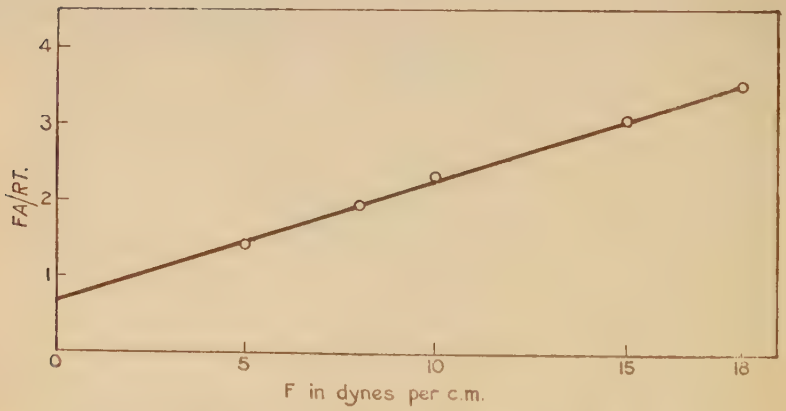
TABLE IV.

Benzene-Water Interface.

F.	S.	$2{\cdot}303\frac{F}{S}=\frac{FA}{RT}$.
1	2·3	1·0
2	3·798	1·21
3	4·985	1·38
4	5·59	1·64
5	6·49	1·77

Fig. 1.

Heptane-Water Interface.



The results given in Tables II. and IV. are shown graphically in figs. 1 and 2. It will be seen that the results can be represented by straight lines, the equation of the straight lines being given by the relation

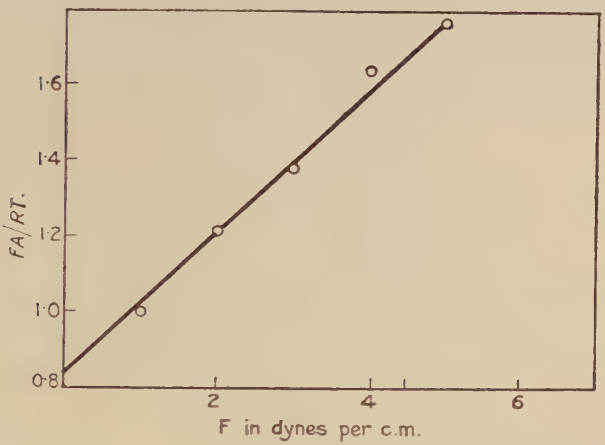
$$\frac{FA}{RT}=\frac{B}{RT}.F+x,$$

where B/RT is the slope of the curve and x the intercept on the FA/RT axis. Thus the values of B and x can be easily determined from the curves. The values of B and x obtained

for the heptane-water interface are $3{\cdot}1 \times 10^9$ and ·75, and those for the benzene-water interface are $4{\cdot}6 \times 10^9$ and ·84. The values of B are appreciably higher than those obtained in other cases, such as butyric acid in a benzene-water interface, and give the corresponding values for the limiting cross-section per molecule as 51×10^{-16} and 75×10^{-16}. If the

Fig. 2.

Benzene-Water Interface.



solutions are considered ideal, then these values can also be calculated from the Gibbs's equation

$$\Gamma = -\frac{d\sigma}{2{\cdot}303\,\mathrm{RT}d\log_{10}\mathrm{C}},$$

where the molecular cross-section would be given by the relation $\frac{1}{\Gamma \mathrm{N}}$, N being the Avogadro constant. The values thus calculated are $57{\cdot}2 \times 10^{-16}$ and 175×10^{-16} *. Such

* The value of $\frac{d\sigma}{d\log \mathrm{C}}$ in the data of Mathews and Stamm does not become a constant in the case of heptane-water interface. The above value of molecular cross-section is calculated from points in the σ-log C curve where the film may be possibly still unimolecular. For higher values of $\frac{d\sigma}{d\log \mathrm{C}}$ the values of the molecular cross-sections are much higher. In the case of benzene-water interface, the value of $\frac{d\sigma}{d\log \mathrm{C}}$ reaches a constant $= 5{\cdot}39$, and this value has been used in the calculation.

large values are very peculiar. Even the values of molecular cross-sections under high compression, as already deduced from the equation of state, are much higher than the minimum area per molecule of the 21·5 Å.U. computed from data on films of palmitic acid. It is also interesting to note from the data of Mathews and Stamm that the value of Γ calculated in the ordinary way from Gibbs's equation does not really reach a limit with increasing concentration of dimethylaniline. It is very probable that at higher surface pressures we are not getting a really monomolecular film, but a film several molecules deep. It is also an interesting fact in this connexion that the equation

$$\frac{FA}{RT} = \frac{B}{RT} \cdot F + x$$

does not hold for pressures nearing the maximum determined in these investigations, though for ordinary pressures it is fairly exact, as the graphs show. At pressures nearing the maximum the value of FA/RT is proportionately less, because the slope of the curve F-$\log_{10}$ C is comparatively high. Evidently the considerations developed by Schofield and Rideal are not applicable to multimolecular films.

Summary and Conclusion.

It is possible, therefore, to draw some interesting conclusions from this investigation. For relatively weak solutions the equation $F(A-B)=xRT$, analogous to that of Amagat connecting the pressure and volume of highly compressed gases, is obeyed by surface films. When, however, the film no longer remains unimolecular the equation does not hold. The films formed at the surface layer may not always be unimolecular, but may be several molecules deep. So long as weak solutions are employed and the films remain unimolecular, the effect on the surface tension is due to their thermal agitation alone. Under these conditions Schofield and Rideal's conclusion that at a given temperature their effectiveness depends solely on their surface concentration, their interfacial areas, and their lateral cohesion seems to be correct.

LXXXIX. *Emissivity Methods of Investigating Thermal Conduction in Metals.* *By* H. Gregory, *Ph.D., A.R.C.S., D.I.C., Assistant Professor in Physics, and* C. T. Archer, *M.Sc., A.R.C.S., D.I.C., Lecturer in Physics* *.

THE present paper aims at a critical discussion of the development of Emissivity Methods of the Measurement of the Thermal Conductivities of Metals.

The basis of such methods is to connect the emission of heat from an electrically-heated wire with the thermal conduction of the material of the wire, and, for the purpose of theoretical discussion, can be represented by the equation:

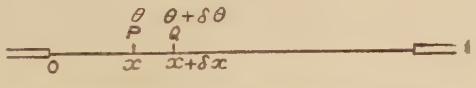
$$K_M A \frac{d^2\theta}{dx^2} + \frac{C^2\rho_\theta}{JA} = H_\epsilon ; \quad . \quad . \quad . \quad . \quad (1)$$

i.e.

$$K_M A \frac{d^2\theta}{dx^2} + \frac{C^2\rho_0(1+\alpha\,.\,\theta)}{JA} = H_\epsilon .$$

This equation in its general form expresses the thermal equlibrium of an element δx of the wire, K_M is the thermal conductivity of the material of the wire, A its cross-sectional area, θ° C. the temperature of the element, x its distance from some origin, C the current strength, ρ_0 and ρ_θ the specific resistances of the material of the wire at the temperatures 0° C. and θ° C., α the temperature coefficient of increase of resistance, and H_ϵ denotes the total loss of heat per unit length from the surface of the element.

Fig. 1.



H_ϵ depends generally on the disposition of the wire with regard to space, and on the nature, extent, and symmetry of the surrounding medium.

It will be necessary to distinguish what the authors would call "controlled emission," in which the loss of heat is controlled by a careful choice of the medium surrounding the wire and by a precise symmetry in the surrounding enclosure.

The emissivity equation has been used by various experimentalists in a form which has been based on a simplification of its theoretical aspect.

* Communicated by the Authors.

In Jaeger and Diesselhorst's * experiments the electrically-heated bar was surrounded by a symmetrical enclosure, the external surface of which, together with the ends of the bar, was maintained at a constant temperature, and the intervening space filled with a lagging material. The authors claimed that such lagging was equivalent to a loss of heat from the surface negligible in comparison with the flow of heat along the bar.

In the state of thermal equilibrium, equation (1) can then be modified to give a relation between the electrical potential and the temperature at a point along the bar. This results in a parabolic distribution of temperature along the bar, and the ratio of the thermal conductivity to the electrical conductivity is expressible as a function of the temperatures and the potentials at three points along the bar.

Although the method was an important advance in the subject, it is open to criticism on the points as to (*a*) how far the supposed loss of heat through the lagging can be regarded as negligible in comparison with the flow of heat along the bar, and (*b*) the accuracy with which the temperatures at points along the bar can be measured by thermocouples sunk into the bar at the appropriate points.

In a later method, proposed by Professor Callendar † and carried into effect by Duncan ‡ in the case of copper, the electrically-heated wire was disposed horizontally in a gaseous atmosphere symmetrical with the wire, the ends of the wire and the enclosure being maintained at a constant temperature.

In this case it was assumed that the loss of heat per unit length from the element of the surface could be expressed by Newton's law :

$$\Pi_\theta = \lambda \,.\, \theta,$$

λ being some constant.

A further simplification of the emissivity equation was introduced in that a current strength was chosen critically from the equation :

$$c^2 = \frac{\lambda A J}{\alpha \rho_0}.$$

This leads to a parabolic distribution of temperature along the wire, and the thermal conductivity K_M is, in this case, expressible as a function of the mean resistance of the

* *Preuss. Akad. Wiss Berlin*, xxxviii. p. 711 (1899).
† Encycl. Brit. 11th Ed., "Conduction of Heat."
‡ McGill Coll. Report, 1899.

wire and the critical value of the current strength found as above.

The authors of the present paper regard such a method in its main aspects as infinitely superior in experimental accuracy to the method of Jaeger and Diesselhorst.

The question now arises: How far can Newton's law be regarded as susceptible of application in the case of such a method?

In 1924, Miss S. M. Marshall and J. O. C. Vick *, acting on a suggestion by Dr. Gregory, commenced a series of experiments in which Newton's law was severely tested, and made an attempt to determine the precise conditions of pressure, and of the nature and extent of the surrounding medium, under which Newton's law was valid in the case of electrically-heated wires. Such conditions have been termed by the authors "controlled."

Their experiments indicate in the clearest possible manner that the "control" conditions required can be effected by a proper choice of (*a*) the radius of the "control" tubes, (*b*) the pressure of the gas surrounding the wire, and (*c*) the excess temperature of the wire over that of its surroundings.

Fig. 2, which refers to a horizontally-disposed system of tubes and which has been taken from the paper referred to, exemplifies these points in the case of two tubes of diameter 0·918 and 2·342 cm. respectively, the diameter of the wire being 0·01538 cm.

Miss Marshall has more recently carried out a series of experiments, using a vertical disposition of tubes and wires in carbon dioxide. In this case it was found that it was necessary to work at pressures as low as from 0·001 to 0·02 mm. as the "control" pressure, and that over this range of pressure a linear relation holds for a range of temperature up to and beyond 100° C.

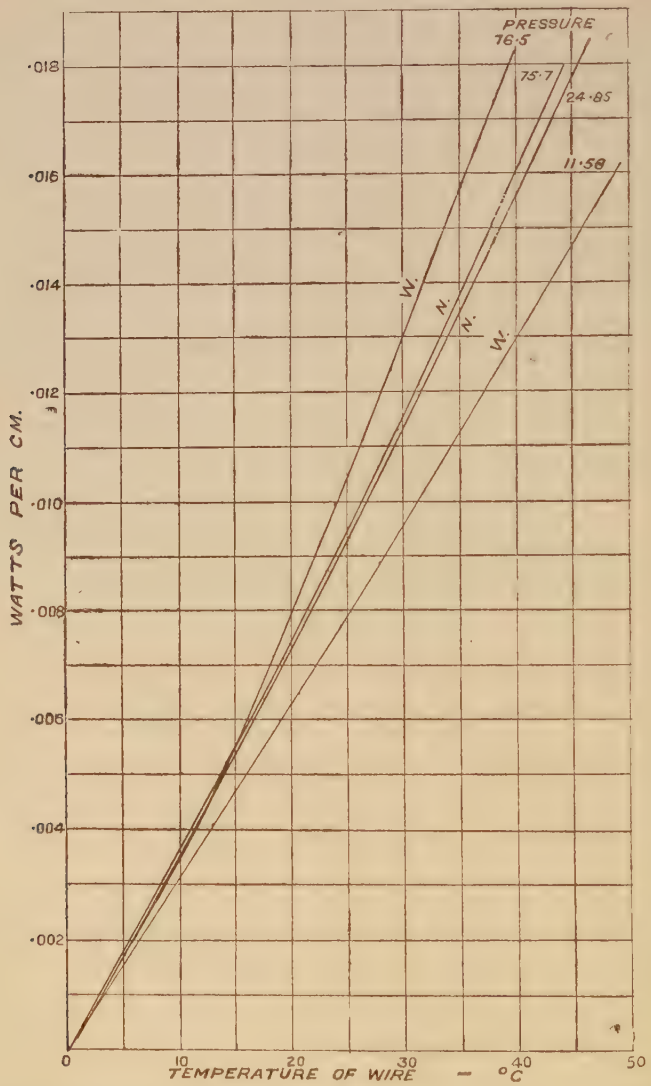
Generally speaking, for "controlled" emission in which the electrically-heated wire is disposed in a gaseous atmosphere bounded by a surface symmetrical with the wire, we have

$$H_e = \frac{2\pi K_g \theta}{\log_e r_2/r_1} + \text{Convective loss,} + \text{Radiation.}$$

The first term represents the loss of heat by conduction through the gas, K_g being the thermal conductivity of the gas which is independent of pressure between certain limits of pressure.

* Proc. Phys. Soc. xxxvii. 5, p. 312 (1925).

Fig. 2.

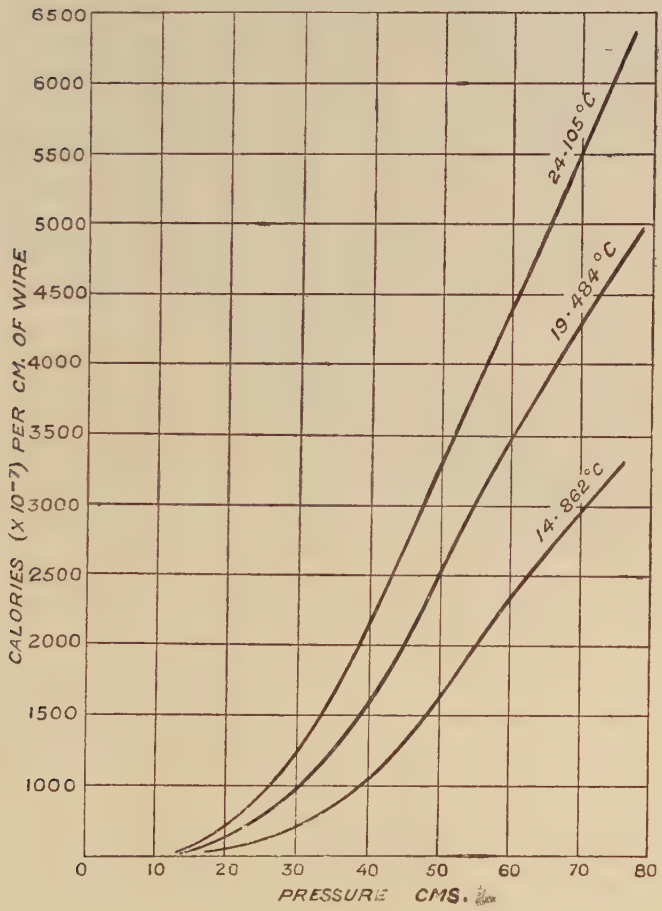


If r_2/r_1 is large, which is the case of an electrically-heated wire coaxial with a tube of large radius, then the loss of heat by conduction is negligibly small and the total loss is mainly due to Convection :

$$H_e = H_c + H_R'.$$

Some aspect of the manner in which the natural convective losses vary with temperature is indicated by the results obtained by the authors on Convection of heat, and fig. 3 refers to the convective losses in a tube of large bore at three different temperatures of the wire.

Fig. 3.



From such results subsidiary curves indicating the variation of convective loss with the temperature of the wire can be drawn as shown in fig. 4. It is indicated that the linear relation between convection and temperature holds

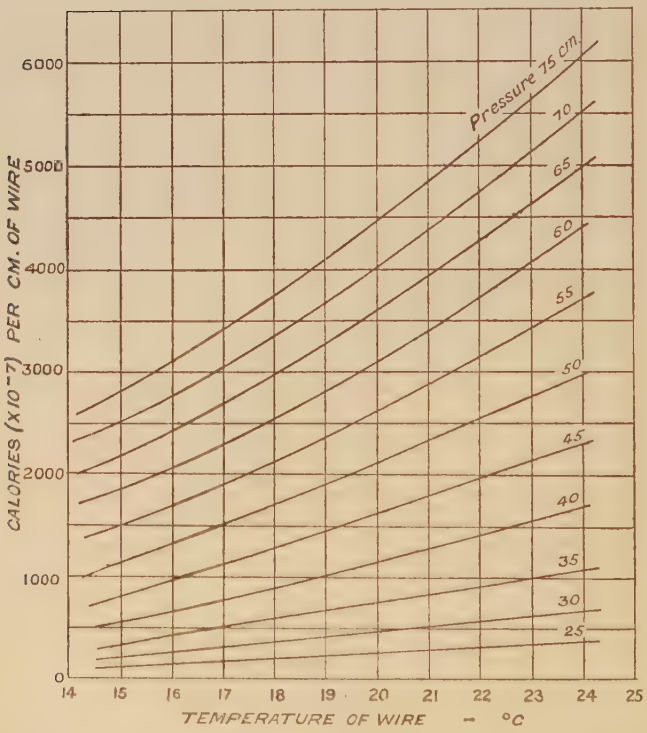
only for a small range of pressures which depends on the diameter of the external tube.

If r_2/r_1 is small the convective losses tend to become negligible, and the total losses are then due mainly to Conduction through the gas.

Here

$$H_\epsilon = \frac{2\pi K_g \theta}{\log_e r_2/r_1} + \text{Radiation.}$$

Fig. 4.



In all cases where r_1 is of the order of 1 to 3 mils the Radiation losses are negligible in comparison with the Conduction losses, and, in any case, can be represented by a term $\mu . \theta$ for a large range of temperatures. H_ϵ will then become independent of pressure, since K_g depends on the pressure only for pressures so low that the Mean Free Path of the gas becomes comparable with the distance between the wire and the wall of the tube. Hence, for a large range

of pressures, provided that the Convective losses are negligible,

$$\begin{aligned} H_\epsilon &= f(\theta), \\ &= \frac{2\pi K_0(1+\alpha\,.\,\theta/2)\theta}{\log_e r_2/r_1} + \mu\,.\,\theta, \\ &= A\,.\,\theta + \beta\,.\,\theta^2. \end{aligned}$$

These conclusions in the case of tubes of narrow bore are substantiated by the results of the experiments of Miss Marshall and Vick on Atmospheric Air.

Miss Marshall, working at low pressures with carbon dioxide has shown that H_ϵ is linear with the temperature of the wire and independent of the radius of the "controlling" tube.

We will assume then, for theoretical purposes, that the emission of heat conforms with Newton's law under some precisely fixed aspect of the "controlling" conditions ; *i. e.*

$$H_\epsilon = \lambda\,.\,\theta,$$

where λ is a constant, and we have

$$\frac{d^2\theta}{dx^2} + \frac{C^2\rho_0(1+\alpha\,.\,\theta)}{JK_MA^2} = \frac{\lambda\,.\,\theta}{K_MA},$$

or

$$\frac{d^2\theta}{dx^2} - \left(\frac{\lambda}{K_MA} - \frac{C^2\rho_0\alpha}{JK_MA^2}\right)\theta = -\frac{C^2\rho_0}{JK_MA^2};$$

i. e.

$$\frac{d^2\theta}{dx^2} - P\,.\,\theta = -Q, \qquad \ldots\ldots \quad (2)$$

where

$$P = \frac{\lambda}{K_MA} - \frac{C^2\rho_0\alpha}{JK_MA^2}$$

and

$$Q = -\frac{C^2\rho_0}{JK_MA^2},$$

ρ_0 being the specific resistance of the material of the wire at 0° C., and α the temperature coefficient of increase of resistance.

The solution of (2) is given by

$$\theta = \frac{Q}{P} + C_1\,.\,e^{\sqrt{P}\,.\,x} + C_2\,.\,e^{-\sqrt{P}\,.\,x},$$

where C_1 and C_2 are constants to be determined by a consideration of the boundary conditions ; θ is zero when x is

zero or equal to $2l$, then

$$C_1 = -\frac{Q}{P}\left(\frac{1-e^{-2l.\sqrt{P}}}{e^{2l.\sqrt{P}}-e^{-2l.\sqrt{P}}}\right)$$

and

$$C_2 = \frac{Q}{P}\left(\frac{1-e^{-2l.\sqrt{P}}}{e^{2l.\sqrt{P}}-e^{-2l.\sqrt{P}}}\right).$$

Now, in actual practice, with the system used by the authors in which air was used in tubes of radius of the order 0·45 cm. with wires of diameter of the order 0·015 cm., $\sqrt{P}$ is of the order 1·7. Hence

$$C_1 = -\frac{Q}{P}e^{-2l.\sqrt{P}}$$

and

$$C_2 = -\frac{Q}{P}.$$

Then

$$\theta = \frac{Q}{P}\{1-e^{\sqrt{P}.(x-2l)}-e^{-\sqrt{P}.x}\}$$

which is the temperature distribution along an electrically-heated wire under "controlled" conditions conforming to Newton's law.

If a system of two tubes and wires exactly similar except in length are used, both being in gaseous connexion and the same electric current flowing through both, then we can discuss, from the above equation, the condition for the equality of temperature distribution along the wire in both tubes.

For the two wires to give the same temperature distribution, we have

$$\int_0^{2l_2}\frac{\rho_0(1+\alpha\theta)\,dx}{A} - \int_0^{2l_1}\frac{\rho_0(1+\alpha\theta)\,dx}{A} = \frac{2\rho_0}{A}(l_2-l_1)\left(1+\alpha\frac{Q}{P}\right),$$

which condition holds if

$$e^{-\sqrt{P}.2l_1} \quad \text{and} \quad e^{-\sqrt{P}.2l_2}$$

are negligibly small compared with unity.

Also, for the equality of the end-effect, the heat conducted along the leading wires is given by

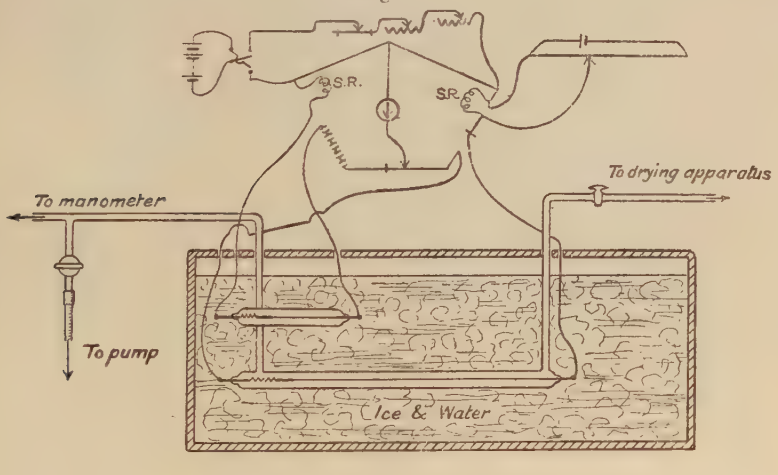
$$K_M A\left(\frac{d\theta}{dx}\right)_{x=0} = \frac{QK_MA}{\sqrt{P}}(1-e^{-\sqrt{P}.2l}),$$

which is the same for both systems if $e^{-\sqrt{P}.2l}$ is negligibly small compared with unity.

The authors made use of such a system to determine the thermal conductivity of platinum. The apparatus was constructed to determine first of all Newton's law constant λ, and to determine the best "control" conditions of pressure and radius of tube which would conform to Newton's law.

The system is indicated diagrammatically in fig. 5. The tubes were of internal radius 0·45 cm., the platinum wire having a diameter of 4 mils, and the system was immersed in a bath of ice and water kept at constant temperature by a system of mechanical stirrers. The wire in the longer tube was connected in series with a standard 1-ohm resistance coil in the main arm of a Callendar-Griffiths bridge;

Fig. 5.



the shorter wire also in series with a similar 1-ohm coil in the compensating arm of the bridge. The tubes were filled with air, dried and freed from carbon dioxide, at atmospheric pressure. The platinum wires having been calibrated previously as a platinum thermometer, the bridge was set to correspond to some predetermined temperature. Then, by means of the variable resistances shown, the current flowing through the system was adjusted until a balance of the bridge was obtained when, the state of thermal equilibrium having been attained, the wire was at the chosen temperature. The value of the current required to maintain thermal equilibrium was then measured by the potentiometer connected to the terminals of the standard resistance coil. Next, the pressure of the air in the tubes was reduced by

using the pumps to about 10 cm. below that of the atmosphere and, if necessary, the strength of current required to maintain thermal equilibrium, *i. e.* the balance of the bridge, was adjusted. Further reductions of pressure were made in stages of about 10 cm., the current strength being measured at each stage, until a pressure was reached such that the mean free path of the gas became comparable with the dimensions of the tubes, when considerable changes in the strength of current required to maintain the temperature of the wire were necessary owing to the variation of the conductivity of the gas with pressure at such pressures. This series of observations was then repeated with different settings of the bridge so that the current strengths required to maintain the wire at several different temperatures varying from 18° C. to about 4° C. were found. It was found that in each case the current strength remained practically constant over a wide range of pressure, loss of heat by convection having been avoided by using tubes of small bore. The total heat-loss was thus due purely to conduction through the gas; and since the thermal conductivity of a gas is independent of the pressure over the range considered, such total loss of heat remained constant. The total heat-loss in each case was then calculated, using the values of the current strengths obtained and the values of the resistance per unit length of wire at the appropriate temperatures, which were found from determinations of the variation of the resistance of the wire with temperature in separate experiments.

The value of the heat loss at each of the different temperatures of the wire was then plotted against the temperature of the wire. The results obtained in a particular case are shown in fig. 6.

From the straight line thus obtained, the value of λ was calculated by observing the slope θ of the line and using the relation $\lambda = \tan\theta$.

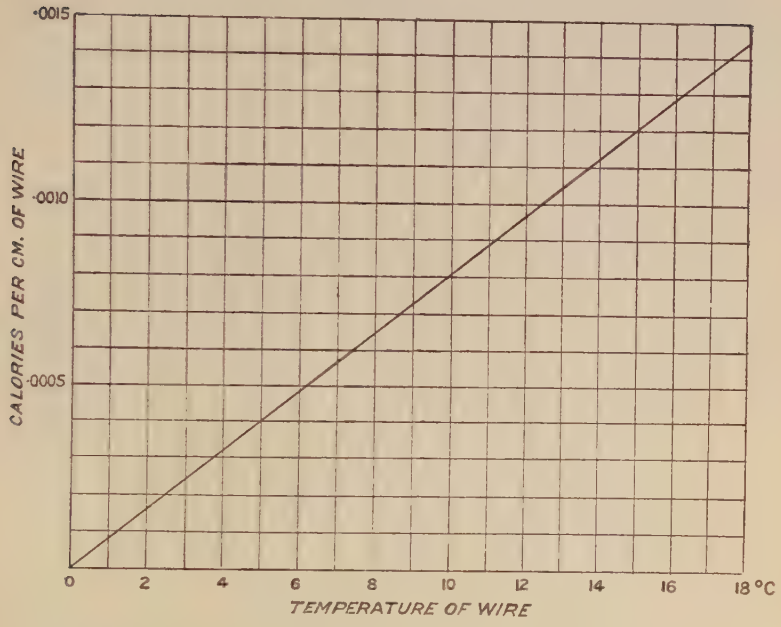
Having obtained the value of λ, the shorter wire was connected alone in the bridge, and its mean resistance was found from the bridge setting for a given strength of current.

The expression from which the value of K_M, the thermal conductivity of the material of the wire, can be found for a temperature corresponding to the mean temperature of the wire is obtained :—

If R_s denote the mean resistance of the shorter wire, then

$$R_s = \int_0^{2l} \rho_0 \left(1 + \alpha \cdot \frac{\theta}{A}\right) dx.$$

Fig. 6.



Substituting the value of θ in terms of x, we have

$$R_s = \int_0^{2l_2} \frac{\rho_0 \left\{ 1 + \alpha \left[\frac{Q}{P} \left(1 - e^{\sqrt{P}(x-2l)} - e^{-\sqrt{P}.x} \right) \right] \right\}}{A} dx,$$

$$= \frac{2l_2\rho_0}{A} + \frac{\rho_0\alpha}{A} \left\{ \frac{2l_2Q}{P} - \frac{2Q}{P} \left(\frac{1}{\sqrt{P}} - \frac{e^{-\sqrt{P}.2l_2}}{P} \right) \right\},$$

$$= \frac{2l_2\rho_0}{A} + \frac{\alpha\rho_0}{A} \left(\frac{2l_2Q}{P} - \frac{2Q}{P^{3/2}} \right),$$

since $e^{-\sqrt{P}.2l_2}$ is negligibly small compared with unity; *i. e.*

$$P^{1/2} = \frac{N}{M},$$

where

$$M = \frac{2Q\alpha\rho_0}{AP}$$

and

$$N = \left(\frac{2l_2\rho_0}{A} + \frac{2Ql_2\rho_0\alpha}{AP} - R_S \right).$$

Hence $$\frac{1}{K_M}\left(\frac{C^2\alpha\rho_0}{JA^2}-\frac{\lambda}{A}\right)=\frac{N^2}{M^2}$$

and

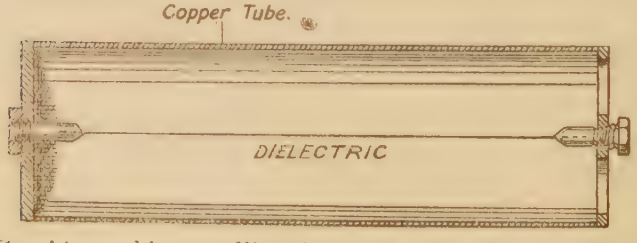
$$K_M=\frac{M^2}{N^2\left(\frac{C^2\rho_0\alpha}{JA^2}-\frac{\lambda}{A}\right)}.$$

The authors found a value for platinum at a mean temperature of 15° C., which compares well enough with previous results. The method can be designed to give fairly accurate results if due attention is paid to a careful choice of the dimensions of the wire and the surrounding tube; and it has the great advantage of incorporating a measurement of λ and fixing the "control" conditions of the system for which Newton's law is valid.

The foregoing method, although applicable to the measurement of the thermal conductivity of metals with fair accuracy, is limited by the range of temperature over which it is possible to work. At high temperatures the departure from Newton's law for the emission of heat would increase the complications; and for the reason that the authors sought to design an experimental system applicable to the measurement of thermal conductivities at high temperatures, they were led to consider a modification of the "control" conditions which promises to be susceptible of greater accuracy and at the same time to be applicable in stricter accuracy to the problem of the variation of thermal conductivity with temperature.

This method will now be treated theoretically.

Fig. 7.



Consider a thin metallic wire to be embedded coaxially in intimate contact with a solid dielectric cylinder of a substance whose thermal conductivity is invariable with temperature. The problem is then similar to the case in which the wire is surrounded by a gaseous medium, the gas being replaced by the dielectric medium.

An important difference exists in the fact that the losses of heat from an element of the wire when in thermal equilibrium are now those due purely to conduction through the dielectric, and can be represented by a term of the form :

$$\frac{2\pi K_s \theta \,.\, \delta x}{\log_e r_2/r_1},$$

where K_s is the thermal conductivity of the dielectric; and this can be written

$$\lambda_s \theta \,.\, \delta x,$$

since K_s is invariable with temperature.

We have now an emission which can be controlled to any extent we may desire, since the heat-loss for any given dielectric depends only on the radius of the cylindrical surface. The replacement by a solid dielectric of the gas in the previous problem obviates the complication which exists in the fixing of the "control" conditions required to conform exactly with Newton's law.

Equation (1) can be written

$$K_M A \frac{d^2\theta}{dx^2} + \frac{C^2\rho_0(1+\alpha \,.\, \theta)}{JA} = \lambda_s \,.\, \theta,$$

where

$$\lambda_s = \frac{2\pi K_s}{\log_e r_2/r_1}.$$

For any specified dielectric, the "control" conditions reduce to a proper choice of the radius of the surrounding medium.

The solution of the equation is of the same form as before, and the thermal conductivity of the material of the wire is calculated from the expression :

$$K_M = \frac{M^2}{N^2\left(\frac{C^2\rho_0\alpha}{JA^2} - \frac{\lambda_s}{A}\right)},$$

where

$$N = \left(\frac{2l_2\rho_0}{A} + \frac{2Ql_2\alpha\rho_0}{AP} - R_s\right),$$

$$M = \frac{2Q\rho_0\alpha}{AP},$$

$$P = \frac{\lambda_s}{K_M A} - \frac{C^2\rho_0\alpha}{JK_M A^2},$$

and

$$Q = \frac{C^2\rho_0}{JK_M A^2}.$$

An alternative method of procedure would be :—
In the equation

$$\frac{d^2\theta}{dx^2} - \left(\frac{\lambda_s}{K_M A} - \frac{C^2\rho_0\alpha}{JK_M A^2}\right)\theta = -\frac{C^2\rho_0}{JK_M A^2},$$

if the current strength is chosen so that it satisfies critically the relation

$$\frac{\lambda_s}{K_M A} = \frac{C^2\rho_0\alpha}{JK_M A^2},$$

i. e.

$$C^2 = \frac{\lambda_s JA}{\rho_0\alpha};$$

then

$$\frac{d^2\theta}{dx^2} = -\frac{C^2\rho_0}{JK_M A^2},$$

the solution of which is

$$\theta = \beta(l \cdot x - \tfrac{1}{2}x^2), \qquad \ldots\ldots (3)$$

where

$$\beta = -\frac{C^2\rho_0}{JK_M A^2}.$$

If R_s denote the mean resistance of the shorter wire under the conditions of the experiment, then

$$R_s = \int_0^{2l} \frac{\rho_0(1+\alpha \cdot \theta)}{A}\, dx.$$

Substituting the value of θ in terms of x from (3) above, we have

$$R_s = \frac{2\beta l^3\rho_0\alpha}{3A} + \frac{2l\rho_0}{A}.$$

Hence, if R_0 is the resistance of the wire at 0° C., and since

$$\beta = -\frac{C^2\rho_0}{JK_M A^2},$$

therefore the conductivity of the material of the wire is given by

$$K_M = \frac{C^2 R_0 l}{6JA(R_s - R_0)},$$

$$= \frac{\pi K R^2_0 l}{3\rho_0\alpha(R_s - R_0)\log_e r_2/r_1}.$$

The authors are at present engaged in experimental work based on the last-named method, in which sulphur has been chosen as the dielectric substance. The results of the investigation will be published in due course.

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XC. *The Characteristics of Gasfilled Photoelectric Cells.* *By* N. R. Campbell. (Communication from the Research Staff of the General Electric Company, Ltd., Wembley.)

Summary.

The relation between the current, the voltage, and the illumination of gasfilled photoelectric cells has been studied in a region which is of great practical importance but has received much less theoretical consideration than the remainder, namely the portion immediately before the potential at which the independent discharge starts.

Spherical and plane cells have been studied; their behaviour, though at first sight different, is essentially similar. In both cases the "limiting curve," or locus of points at which the light-controlled discharge passes into one almost independent of the light, consists of two parts, on the upper of which the passage between the two forms of discharge is continuous and stable, and the magnification of the primary photoelectric current by the discharge is very much greater than on the lower. The difference between the two types of cell is that illuminations which are practically important lie wholly on the lower portion in the spherical cell but not in the plane cell. Some practical conclusions are deduced.

An attempt is made to explain the varying forms of the upper ends of the characteristics. For this purpose the portion of the characteristic which is normally unstable is studied by placing a current-limiting device in series with the cell. The main features seem to accord with expectation based on the accepted theory of the glow-discharge, but there are minor features which present some difficulty. The unstable portion of the characteristic may be used for measuring small illuminations.

Introduction.

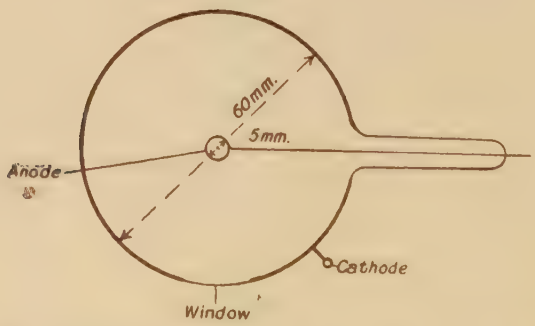
THE general form of the current-voltage characteristic of a gasfilled photoelectric cell is well known and understood; it provided the original basis of Townsend's theory of ionization by collision. The characteristic is terminated at the upper end by the passage of the discharge from the form in which it is supported by the photoelectric emission of electrons at the cathode, and in which the current at a

given voltage is approximately proportional to the incident light, to the form in which it is unsupported and the current almost independent of the light. The change from one form to the other is usually accompanied by a large and sudden increase in current, and it is irreversible; a small reduction of the voltage or removal of the light does not restore the original form. For practical purposes, the important part of the characteristic is that near the upper end, and a limit to the sensitivity of the cell is set by the change of form; this part of the characteristic is less well known and understood. Townsend's theory takes no account of electrons liberated at the cathode by the impact of positive ions; and it is this impact which doubtless plays the main part in determining the starting potential of the unsupported discharge, in the presence, as in the absence, of photoelectric action at the cathode. Accordingly an investigation of the upper termination of the characteristic has been undertaken, which appears to have some theoretical as well as practical interest.

Cells investigated.

The cells investigated had all cathodes of potassium "sensitized" by the Elster and Geitel method of the discharge in hydrogen, and were filled with argon containing about 1 per cent. of nitrogen. Some observations were

Fig. 1 *a*.

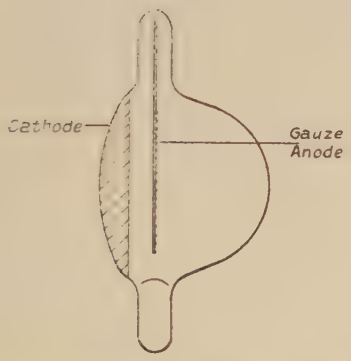


made also with the helium-neon mixture derived from the fractionation of air; but as the results were qualitatively similar, no further reference to them will be made. The cells were of two types, shown in figs. 1 *a* and 1 *b*; the first will be called spherical, the second plane. The first is the type that has hitherto been usually adopted in the construction of photoelectric cells; but cells of the second

type have been introduced by Otto Pressler, of Leipzig, and were recently described by Schroeter *.

It has often been remarked that the current through a gasfilled cell with constant voltage and constant illumination is not constant, but changes slowly with time. Part of this change, characteristic of some cells on the market, can be avoided by proper conduct of the process of sensitization ;

Fig. 1*b*.



but part seems an unavoidable consequence of some regular action of the discharge upon the cathode, and is similar to changes known to occur in discharge vessels of all types ; it is represented with some accuracy by a shift of the whole upper end of the characteristic parallel to the axis of voltage. The change makes accurate measurements impossible, but can be allowed for partially by referring all voltage measurements to that required to produce a fixed current with a fixed illumination, measured immediately before and afterwards, and assigning to this standard a mean value. However, the uncertainty in any well-constructed cell is insufficient to throw doubt on the results presented here.

Characteristics of Plane Cell.

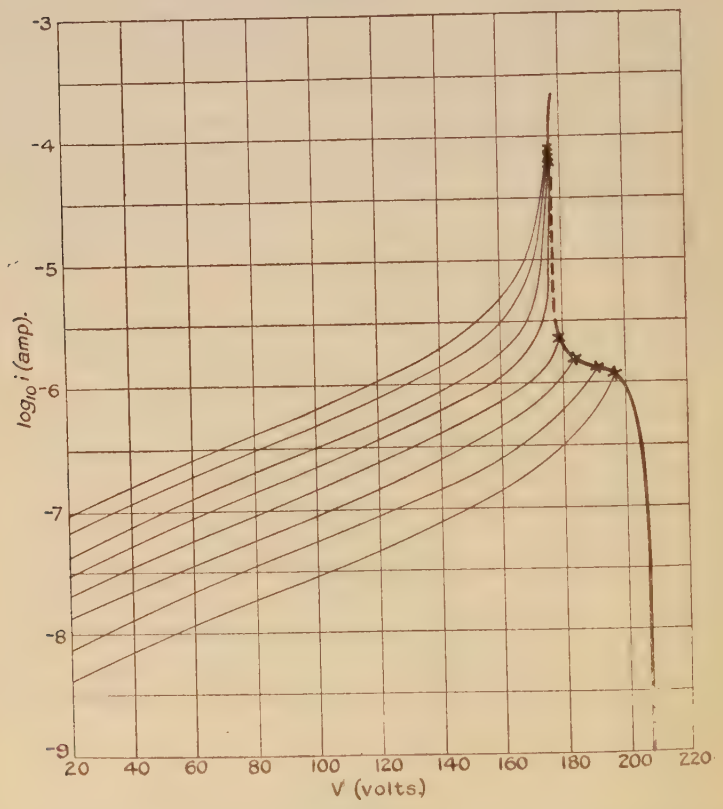
The results for a plane cell filled to a pressure of 0·18 mm. are shown in fig. 2, where, in order to save space, the logarithm of the current is plotted against the voltage. The set of nearly straight and parallel lines are the characteristics of the cell under different illuminations ; they terminate at the points marked × by the occurrence of

* F. Schroeter, *Zeit. f. Tech. Phys.* vii. p. 417 (1926).

an unsupported discharge; these terminations are joined by the thick curve, of which the middle portion is dotted because it cannot be actually observed.

The thick curve is a definite characteristic of the cell, and will be called the *limiting curve*. It divides the diagram into two parts—that on the left being the region of which each point represents a discharge which can be obtained at

Fig. 2.



some voltage and at some illumination, and which stops when the light is turned off; that on the right represents discharges which are either unstable or do not stop when the light is turned off. The curve, as might be expected from its form, falls into two parts distinguished by the nature of the termination. When a characteristic such as A, corresponding to relatively low illumination, meets the lower part of the limiting curve, a large and sudden increase of

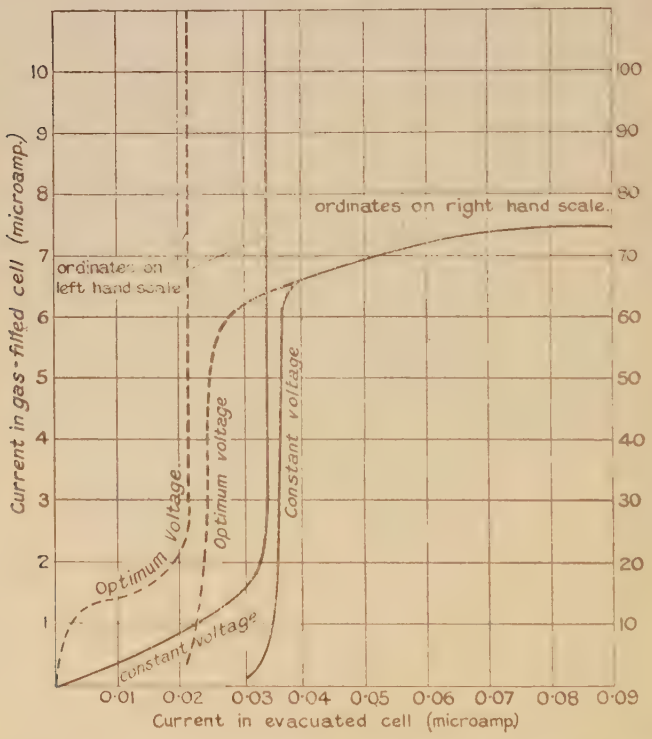
current occurs which is not reversed when the potential is again reduced ; this is the form of termination familiar to all users of these cells. But when a characteristic such as B, corresponding to relatively high illumination, meets the upper part of the limiting curve, there is no discontinuity ; in the neighbourhood of ×, as elsewhere, the current is a smooth, single-valued function of the voltage ; the fact that the limiting curve has been reached can be ascertained only by turning off the light and observing that the current does not fall to zero. The termination of a characteristic which, in its lower portion, lies between those which meet the upper and lower portions of the limiting curve is indefinite; when the characteristic approaches the limiting curve, the current "kicks" irregularly, and no readings can be taken : this condition persists over a range of illumination amounting to about 10 per cent.

These facts are obviously important in the use of the cell. The voltage to be applied to it may be chosen so that the termination is never reached whatever the illumination. The greatest voltage that can then be used is that corresponding to the vertical dotted portion of the limiting curve. On the other hand, if the maximum illumination to which the cell is to be subjected is known, the greatest voltage is that corresponding to the intersection of the limiting curve with the characteristic representing this illumination. If the first alternative is adopted, the relation between the current and the incident light is shown by the "constant voltage" curve of fig. 3 ; here the current through the gas-filled cell is plotted against that which flows through the same cell when evacuated ; this last value is very nearly proportional to the illumination if the spectral distribution is unaltered.

Such curves represent the behaviour of the cell when used to measure light. But sometimes, especially in modern technology, a cell is used merely to indicate a change from light to darkness, the light being approximately constant in intensity. The voltage chosen is then that appropriate to this light, and the question is important how the resulting current varies if the light is changed, the voltage being always adjusted to the optimum. The answer is given by the curve in fig. 3 marked "optimum voltage." The features of the curve to be observed are that at low illuminations the current is proportional to the illumination, at high illuminations almost independent of it; between these two portions is a region in which the current varies very rapidly with the illumination. The steepest part of the curve cannot be realized ; for these illuminations a rather lower voltage

would have to be employed; but a 25-fold increase in current for 25 per cent. increase in illumination can actually be observed. It is important to notice that the region in which the current increases very rapidly with the light separates two regions in which it varies but slightly with the light. Ignorance of this fact might lead to great sacrifice of efficiency; when it was found that an increase of the light beyond a certain point gave little increase in

Fig. 3.

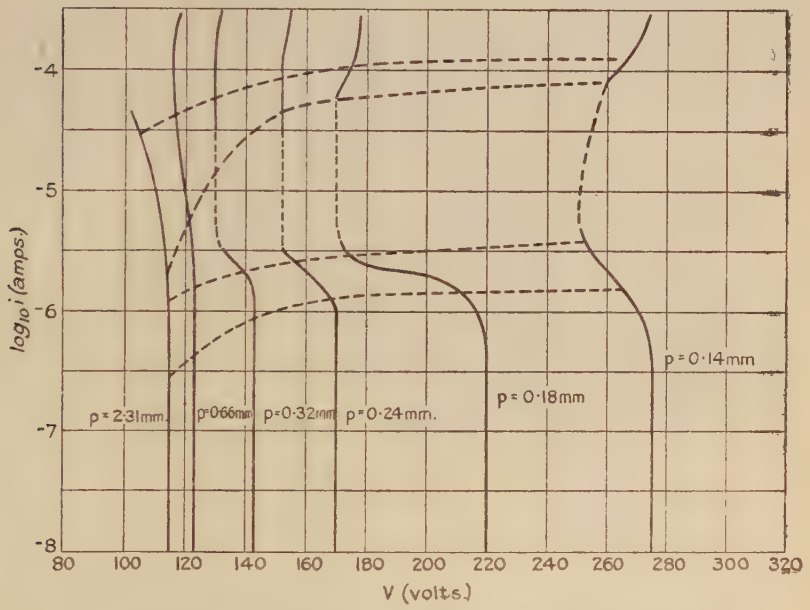


current, it might not be suspected that a further increase of light would produce an enormous increase in current. The illumination at which the great increase occurs in cells of this type is not at all impracticable; in that to which fig. 3 refers about 0·05 lumens were entering the cell from a 60-watt gasfilled lamp.

Fig. 4 shows the limiting curves for various pressures of the gas; it does not refer to the same cell as fig. 2, but to one of closely similar construction. The dotted lines in

this diagram pass through points corresponding to equal illuminations. It will be seen that, in general, the maximum current obtainable with a given illumination does not vary greatly with the pressure : but at the higher pressures there is a tendency for this maximum to increase with decreasing pressure. However, the change only becomes important when it leads to the point corresponding to a given illumination transferring itself from the lower to the upper branch of the limiting curve. If cells are tested for maximum

Fig. 4.



current with an illumination in this critical neighbourhood, the most minute changes in the pressure or the construction of the cell may lead to enormous changes in this current.

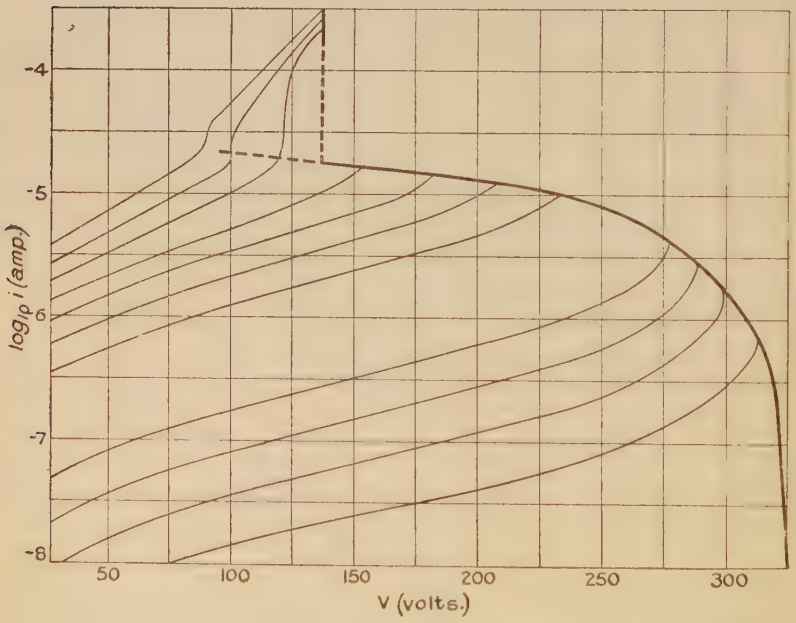
If the pressure is reduced below the lowest value shown in fig. 4, the limiting curve vanishes, for there is no sparking potential and the current never vanishes completely when the light is turned out, except possibly at very small voltages. If the cell is in the dark, or at least exposed to an illumination much less than that which can be detected by the eye, and the potential across it is raised, the current starts at a value not greater than 10^{-9} amp., increases continuously, and returns through the same values when the potential is

reduced. This part of the behaviour of the cell has not yet been investigated in detail.

Characteristics of the Spherical Cell.

Fig. 5 shows the characteristics and limiting curve of a spherical cell filled to a pressure of 0·18 mm. The general shape is the same, but the proportion of the parts is different and the upper and lower portions now intersect at a finite angle. The dotted continuation of the lower part beyond its intersection with the upper is of some interest; along

Fig. 5.



this line the current through the cell undergoes a large and sudden increase when a characteristic meets this continuation, which is not reversed by a slight reduction of voltage, but the current still stops when the light is turned out; the characteristic is unstable in respect of changes of voltage, but not in respect of changes of illumination.

A further and practically important difference between the two types of cell lies in the illumination which corresponds to the change from the lower to the upper part of the limiting curve. In the spherical type this illumination

is about 100 times as great as in the plane type; it lies beyond the region which is practically important for most purposes. For small illuminations, which lie on the lower part of the limiting curve both for the spherical cell and plane cell, the currents through the plane cell are somewhat greater: but the superiority of the latter is enormous for the rather larger illuminations which lie on the upper part of the plane-cell curve and the lower part of the spherical; these illuminations are important in many technical applications. The only purpose for which the spherical type seems preferable is the measurement of small, but not too small, illuminations: for the current through the spherical cell at constant voltage is proportional to the illumination over a greater range. It is noteworthy that even when the cells are evacuated the spherical type is not remarkably superior to the plane type. The original purpose of the spherical cathode with a relatively small window was to secure that the light suffered many reflexions at the active surface, and therefore much absorption, before emergence. If the active metal is unsensitized and brightly metallic, considerable gain in effective sensitivity is secured by this means; but the dull dark surface of the sensitized metal is so little reflecting that there is little gain in increasing the number of possible reflexions. However, it is hoped to discuss this and other matters relating to the sensitized surface in a later communication.

Theory of the Characteristics.

The explanation of the general form of the limiting curve is obvious. The lower part of it represents the sparking potential of the gas, diminished by an emission of electrons from the cathode independent of the impact of positive ions. This diminution (which, of course, has long been known) accords well with the accepted theory of the discharge, especially as expounded by Guenther-Schulze * and by Seeliger and Schmekel †.

The difference between the glow-discharge, characterized by a cathode fall, and the Townsend discharge below the sparking potential, supported by photoelectric emis ion at the cathode, is that in the former the field is distorted, and increased near the cathode, by the development of an appreciable space-charge in virtue of the relatively high-current density. The sparking potential, on the other hand, represents an undistorted field so great that the emission of

* A. Guenther-Schulze, *Zeit. f. Phys.* xxxiii. p. 810 (1925).

† R. Seeliger and J. Schmekel, *Phys. Zeit.* xxvi. p. 471 (1925).

each electron from the cathode leads, through the impact of positive ions produced by it, to the emission of just more than one secondary electron. The Townsend discharge is therefore unstable; the current immediately rises to values for which the space-charge is important, and is ultimately limited by the recombination of electrons with positive ions in the glow-discharge.

Let a photoelectric emission of p electrons per second be excited at the cathode, and a potential V supplied so that $\beta = f(V) < 1$ is the number of secondaries due to each primary electron. Then a steady state will be reached in which the number of primary electrons leaving the cathode in time dt is $p\,dt$, that of the secondaries $\beta p\,dt$, of the tertiaries $\beta^2\,dt$, and so on; the total number will be

$$p\,dt(1+\beta+\beta^2+\ldots) = p\,dt/(1-\beta).$$

The electron current should be proportional to the photoelectric emission at any constant V; the total current, according to Townsend's theory, should be proportional to the electron current in this region. But when the sparking potential V_s is reached, for which $\beta = 1$, the current will increase indefinitely for all values of p. The curves of figs. 2 and 5 show, however, that the current rises more rapidly than the photoelectric emission at values of V less than V_s. The rise must be attributed to the distortion of the field by a space-charge which increases β for a given V by an amount depending on the total current, and therefore upon p. The value V_s for which $\beta = 1$ is reduced as p rises; at constant V the current rises more rapidly than p; the curvature of the characteristics of the cell and the lowering of the sparking potential are two manifestations of the same action.

The explanation of the upper part of the limiting curve is equally simple. Here the primary current is so great that the space-charge is well developed when β is much less than 1. Before β becomes 1 the current is limited by the recombination of ions rather than by the emission of electrons from the cathode; the current is not even approximately proportional to the photoelectric emission—it is more nearly independent of it. There is, therefore, no marked increase of current when β actually becomes 1 and the current is now able to maintain itself independently of the primary emission.

Unstable Portions of the Characteristic.

Seeliger and Schmeckel (*loc. cit.*) were led to insist on the difference between the glow and the Townsend discharge

by observing a form of discharge which seemed intermediate between them. The characteristic of an independent discharge, as usually traced, consists of the voltage axis (*i. e.* zero current) up to the starting potential, together with a continuous portion limited at one end by the potential at which the discharge cannot be maintained (the stopping potential V_g), and at the other by the occurrence of an arc. But Ryde * has shown that, in the rare gases at least, there is an intermediate portion which is unstable and can only be realized if some stabilizing arrangement is included in the circuit, while Seeliger and Schmekel, also Schmierer †, observed another stable portion below the unstable portion.

It seemed, therefore, of interest to trace the complete characteristic of the cells, both in the dark and with photoelectric emission. The lowest part has already been given in figs. 2 and 5 for various amounts of light. In fig. 6 the complete characteristic, up to V_g and beyond, is shown for a spherical cell, and in fig. 7 for a plane cell. The curves were obtained by placing a thermionic valve, acting as a current limiter, in series with the cell and an electrostatic voltmeter across it.

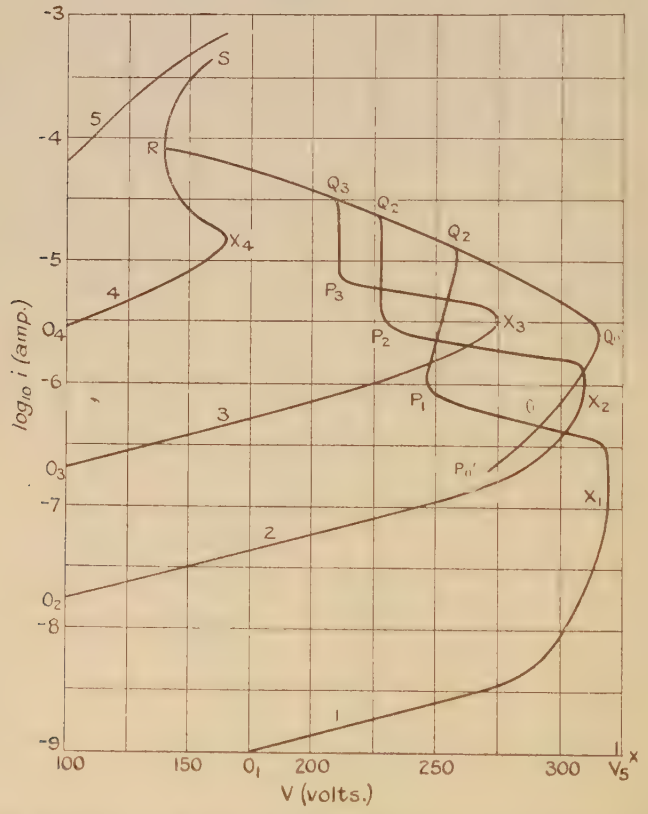
Let us consider fig. 6 first. Curves 1, 2, 3 refer to illuminations such that the characteristic curve meets the lower portion of the limiting curve. They are all of the same form. The bottom portions from O to X, in which the current increases with the potential, are stable, and are nothing but the characteristics shown in fig. 5. They terminate on the limiting curve when they become vertical at the points marked X. (These points do not lie exactly on the limiting curve of fig. 5 ; it is impossible to repeat measurements exactly from day to day.) There is then an unstable portion in which the current rises slightly during a considerable fall of potential. This part, on our theory, represents the development of the space-charge and the increase of β for a given V. It ends at P in a nearly vertical portion. The readings on this portion are irregular and its precise form is uncertain ; but it seems to be just unstable for large illuminations and just stable for small. Here, presumably, the space-charge is fully developed ; β is 1 again and approximately independent of the current, just as it was with the space-charge very slightly developed in the neighbourhood of X ; any currents within certain limits can therefore pass with very nearly the same potential. At

* J. W. Ryde, 'Nature,' cxii. p. 944 (1923).
† J. M. Schmierer, *Zeit. f. Tech. Phys.* vi. p. 370 (1925).

Q, however, an upper limit is set to the current by recombination ; the remainder of the curve Q, R, S is the same for all illuminations, because the current is limited by recombination rather than by emission at the cathode.

But here a difficulty arises. When the space-charge is fully developed and the current is limited by recombination, we ought to have reached the condition of the independent

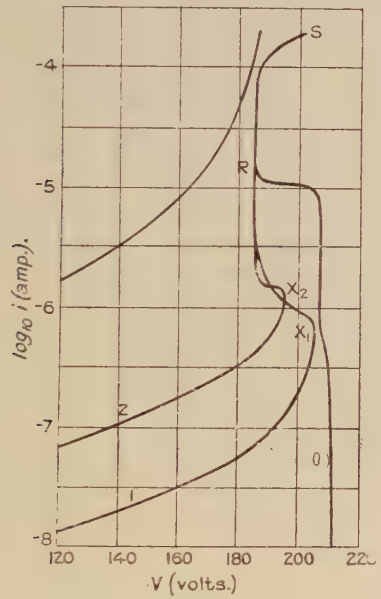
Fig. 6.



glow-discharge. But we have not : that condition is reached at R when $V = V_g$, and is represented by the final stable portion RS. Again—to put the matter another way—if we explain the portions XPQ of the curves as due to the development of the space-charge, how are we to explain the portion QRS, which is very similar in form ? No definite answer can be given at present. If the general outline of

the theory is correct, the conclusion must be drawn that the space-charge is developed in two stages. An attempt has been made to investigate the matter theoretically by determining the distortion of the field by the positive ions at various points of the characteristic; but the uncertainty concerning two important facts, namely the proportion of the current carried by positive ions and the speed of these ions, is so great that a result could hardly be expected.

Fig. 7.



But two experimental facts may be recorded. If a telephone is placed in the circuit, it is found that all through the unstable portion of the characteristic from X to R the current is oscillatory or intermittent; nevertheless the curve is quite definite throughout most of its length, and almost, if not quite, independent of the external voltage applied to the circuit. Again the form of the unstable part of the characteristic seems to be influenced profoundly by the form of the anode. In the plane cell (fig. 7) there is no sign of two discontinuities in the curves 1 and 2 which refer to corresponding illuminations; the portion corresponding to OX in fig. 6 seems to join directly the portion corresponding to PQR. But too much weight must not be placed

on this difference ; the measurements in the plane cell are more difficult because the whole range of potential is much less. Further, since the anode is a gauze, matters may be greatly complicated by the ionization which undoubtedly occurs in the weak fields beyond the anode. Preliminary attempts have been made to investigate the matter by using different anodes in spherical cells ; but the variations between cells apparently similar is so great that it has been difficult to establish more than the fact of a connexion between the size of the anode and the form of the characteristic.

We have so far considered only the characteristics 1, 2, 3 in fig. 6. The whole characteristic 5 is stable, and nothing appears which has not already been seen in fig. 5 ; it does not meet the remainder of the characteristics at all, because the space-charge of the cathode fall develops before the potential becomes so great that $\beta = 1$. In 4 the central and puzzling portion of the characteristic disappears ; the curve proceeds straight from the sparking potential X to the end of the glow-discharge at R. It is obviously hopeless to explain why this portion should disappear at higher illuminations before explaining why it ever appears.

There remains the characteristic 0 for no illumination. Here there is one point of some interest. If this stood alone, it would be natural to identify the portion $P_0'Q_0$ with the portion OX of the other curves, and Q_0 with the sparking potential. Seeliger and Schmekel seem to have identified it so, when they speak of it as being the Townsend discharge *, for OX is the characteristic which Townsend studied. But on comparing 0 with the other characteristics, it is clear that Q_0 corresponds to the other points similarly denoted and that $P_0'Q_0$ corresponds to part of P_1Q_1 ; like them it is oscillatory. The point P_0 corresponding to the other P's cannot be observed ; as we proceed from Q_0 towards P_0' the discharge becomes irregular, owing to a decrease in the period of oscillation, and the instruments move wildly ; it has already been noted that there is difficulty in observing the portions PQ of all the curves. The real P_0 must lie on the voltage axis, probably at the origin, and the portion O_0X_0 must be the axis up to the true starting potential V_s.

It may be noted that in fig. 7, referring to the plane cell, the characteristic 0 for zero illumination is again exceptional. The knee in the curve cannot correspond to the points X on

* *Note added later.*—It is not certain, however, that P_0Q_0 is part of the characteristic which Seeliger and Schmekel studied. The characteristic for zero illumination has been found to vary considerably with the exact form of the cell and the gas-pressure ; and the discharge tubes they used were very different from those to which fig. 6 refers.

the other curves: if there is any discontinuity in them corresponding to this knee, it must be concealed in the almost vertical portion. The difference between the curves for the two types of cell may not therefore be so great as was suggested above.

Practical Use of the Unstable Characteristic.

The characteristic 1 in fig. 6 corresponds to a very small illumination, measurable with an error of about 25 per cent. on a galvanometer giving one scale-division for 10^{-9} amp. And yet the unstable portion of it differs very notably from that corresponding to zero illumination, even in the upper part of the diagram, when the current is several micro-amperes. This difference may be used conveniently to measure, or at least to indicate, very small illuminations. The cell is connected in series with a thermionic current limiter, and in parallel with an electrostatic voltmeter of a commercial type; the voltage applied to the whole circuit is approximately that of the sparking potential in the dark. The current in the current limiter can then be adjusted so that this very feeble illumination produces a change of at least 10 volts on the voltmeter. There is no trouble about insulation, and the voltages concerned are in the neighbourhood of 300 volts, where easily-constructed electrostatic instruments are most sensitive.

The change in voltage can also be amplified very easily by means of a valve; but it must be remembered that it is oscillatory or intermittent. For this reason the method cannot be applied to detect very rapid variations in light, for the frequency of the variations must obviously be less than those of the oscillations. It is hoped to discuss more fully elsewhere the possibilities thus disclosed of increasing very greatly the effective sensitivity of gas-filled cells.

XCI. *A Note on Distortionless Telephonic and Telegraphic Transmission.* *By* A. C. Bartlett. (Communication from the Research Staff of the General Electric Co., Ltd., Wembley.)

In an actual telephone line distortion occurs owing to two causes: waves of different frequencies are in general attenuated in different degrees in passing along the line, and in addition their relative phase-relations change. The only exception to this statement is provided by the Heaviside Distortionless Line, in which R, L, C, and S, the resistance,

inductance, capacity, and leakance respectively per unit length, are such that

$$RC = LS.$$

It is therefore of interest to know if in any case there exists a network that, when associated with a uniform line, gives an exact solution of the problem of rendering the line distortionless. It is the purpose of this note to show that in the simple case of the uniform line, having $S = 0$, such a network can be devised, though it requires a double infinity of simple impedance elements and considerably increases the attenuation.

Taking the case of the uniform line without leakage: its propagation constant is $\alpha + j\beta$, where

$$\alpha + j\beta = \sqrt{(R + jpL)jpC}.$$

$$\alpha = \sqrt{\tfrac{1}{2}Cp\{\sqrt{R^2 + p^2L^2} - Lp\}},$$

$$\beta = \sqrt{\tfrac{1}{2}Cp\{\sqrt{R^2 + p^2L^2} + Lp\}}$$

α can be written as

$$\frac{CR}{\sqrt{LC}} - f_1(p),$$

and β as

$$p\sqrt{LC} - f_2(p),$$

where $f_1(p)$ and $f_2(p)$ are functions of frequency.

Suppose an artificial line could be constructed having the same characteristic impedance

$$Z_0 = \sqrt{\frac{R + jpL}{jpC}}$$

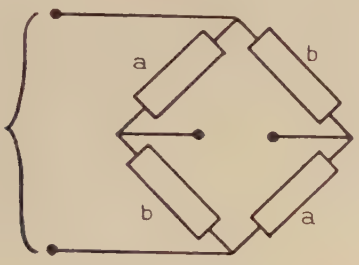
as the uniform line, and having a propagation constant $l(f_1(p) + f_2(p))$, and that this artificial line were inserted in a length l of the uniform line. Then the combination would have a characteristic impedance Z_0, and its combined propagation constant would be

$$l\left(\frac{CR}{\sqrt{LC}} + jp\sqrt{LC}\right),$$

and therefore it would be distortionless in the sense that, if terminated by Z_0, either current or voltage waves are transmitted without distortion.

Putting $f_1(p) + jf_2(p) = \phi$, a network such as fig. 1 would therefore constitute the required artificial line.

Fig. 1.



$$a = Z_0 \coth \frac{l\phi}{2}. \qquad b = Z_0 \tanh \frac{l\phi}{2}.$$

It therefore remains to be seen whether the impedances $Z_0 \tanh \frac{l\phi}{2}$ and $Z_0 \coth \frac{l\phi}{2}$ can be put into physically realizable forms.

It has, however, already been shown * that, provided $Z_0\phi$ and Z_0/ϕ can be put into physical form, then both $Z_0 \coth \frac{l\phi}{2}$ and $Z_0 \tanh \frac{l\phi}{2}$ can be realized physically in a number of ways, each of which employs a single infinity of numerical multiples of $Z_0\phi$ and Z_0/ϕ. The problem therefore reduces to determining whether $Z_0\phi$ and Z_0/ϕ can be physically realized.

Now $$\phi = \frac{CR}{\sqrt{LC}} + jp\sqrt{LC} - \sqrt{(R+jpL)jpC},$$

$$Z_0\phi = \sqrt{\frac{R+jpL}{jpC}} \cdot \phi$$

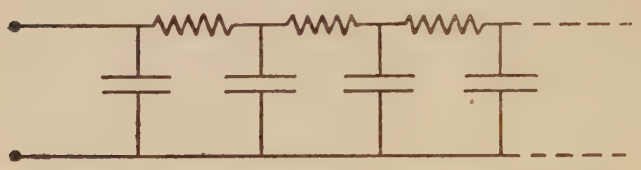
$$= \sqrt{\frac{C}{L}}\,(R+jpL)\left\{\sqrt{\frac{R+jpL}{jpC}} - \sqrt{\frac{L}{C}}\right\}.$$

But $$\sqrt{\frac{R+jpL}{jpC}} - \sqrt{\frac{L}{C}}$$

* Phil. Mag. Nov. 1924, p. 859.

is the impedance of the infinite network shown in fig. 2, where all the resistances have the value $2\sqrt{L/C}$ and the capacities the value $\frac{2\sqrt{LC}}{R}$.

Fig. 2.

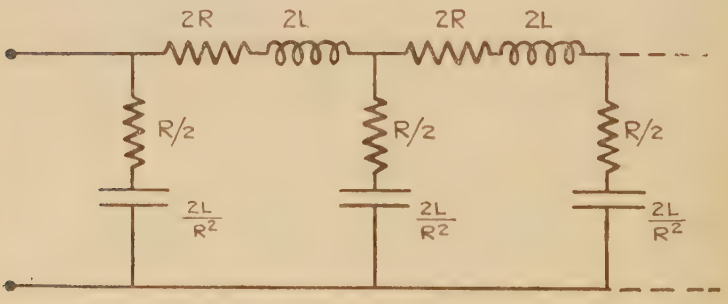


By multiplying all the impedances of this network by

$$(R+jpL)\cdot\sqrt{\frac{C}{L}},$$

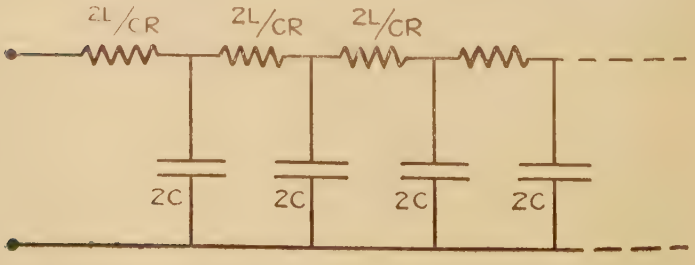
it is seen that $Z_0\phi$ is the impedance of the infinite network shown in fig. 3.

Fig. 3.



In a similar way Z_0/ϕ is the impedance of the infinite network shown in fig. 4.

Fig. 4.



Thus both the impedances

$$Z_0 \coth \frac{l\phi}{2} \quad \text{and} \quad Z_0 \tanh \frac{l\phi}{2}$$

can be physically realized; a double infinity of simple impedance elements, however, is required, but all the infinite networks are convergent, and approximations might be made.

XCII. *On the Variation of the Atom Form Factor with the Wave-length of the Scattered Radiation.* *By* GILBERT GREENWOOD, *M.Sc.**

Introduction.

ONE of the most interesting and important problems which confronts the X-ray analyst of crystal structures, is that of the scattering power of the atoms which form the crystal. In the earliest work this scattering power was taken as a constant and proportional to the atomic weight of the particular atom. Later it was considered as proportional to the atomic number and sometimes, when the atoms were known to be in an ionized state, proportional to the atomic number plus or minus the number of electrons, demanded by the ionization. It was soon realized, however, that this scattering power is not a constant, but varies with the angle of scattering. On the experimental side, evidence of this was brought forward by Debye and Scherrer† in 1918 in their work on diamond powder. An exhaustive research on rocksalt was carried out by Bragg, James, and Bosanquet‡, who measured the scattering powers of sodium and chlorine atoms for different angles using a wave-length of $0{\cdot}616 \times 10^{-8}$ cm. This same general effect—the falling off in the value of F with angle, where F represents the scattering power—was again noticed by Bradley§ for the oxygen atoms in $LiKSO_4$ and by James and Wood‖ in their work on the barytes crystal. Measurements of the F-curves for calcium and fluorine have been carried out by James and Randall¶, using $MoK\alpha$ radiation. This question

* Communicated by Prof. W. L. Bragg, F.R.S.
† *Phys. Zeit.* xix. pp. 474–483 (1918).
‡ Phil. Mag. xlii. p. 1 (1921); xliv. p. 433 (1922).
§ Phil. Mag. xlix. p. 1225 (1925).
‖ Proc. Roy. Soc. A. cix. p. 598 (1925).
¶ Phil. Mag. i. p. 1202 (1926).

has been considered theoretically by Darwin *, Compton †, and Hartree ‡, and the latter has calculated the F curves for a number of different ions. The reason for this falling off in the F-value is to be found in the fact that the scattering electrons are not concentrated in one point but distributed throughout a definite volume. If each electron scatters independently, the resulting scattered beam will be compounded of a series of scattered beams, between which phase differences will exist, and will thus be decreased in intensity. Using the knowledge of electron orbits and intra-atomic structure obtained from the numerical analysis of optical and X-ray spectra, Hartree has calculated this effect for a number of ions. He finds, as in the other theoretical calculations, that in general F depends on θ and λ, being, in fact, a function of $\frac{\sin\theta}{\lambda}$.

The experimental work, carried out up to the present, has chiefly been concerned with the dependence of F on θ. It seemed to be of importance to make some observations on the variation of this factor with wave-length. According to Hartree, F is a function of $\frac{\sin\theta}{\lambda}$, *i. e.* of $\frac{m}{d}$, where m is the order of the spectrum, therefore whatever the wave-length used, the value of F for any reflexion $(h\,k\,l)$ from a certain crystal should be the same. Hence if F is measured, using different wave-lengths, and the results plotted against $\frac{\sin\theta}{\lambda}$ or $\frac{m}{d}$, the curves for the different wave-lengths should coincide.

Discussion of the Method used.

The general scheme of the method was to make Debye-Scherrer photographs of crystals composed of light elements, using radiations of long wave-length, to measure the intensities of the Debye-Scherrer lines photometrically, to apply any necessary corrections, and then to calculate the F-curves from the intensities thus obtained. Many photographs were made from aluminium and from diamond. It was found difficult to obtain a photograph which gave a reliable photometric record (this point is discussed in great detail in the section dealing with the photometry), and in the final results

* Phil. Mag. xxvii. p. 315 (1914).
† Phys. Rev. ser. 2, ix. p. 29 (1917).
‡ Phil. Mag. l. p. 289 (1925).

only the photographs made with the powder scattering CuKα and FeKα radiation were used. An absolute measure of the F-values is, thus, not obtained, but to make all the values comparable the value of F_{111} was taken as unity (on a quite arbitrary scale of course) and all other values were expressed as fractions of this. The following considerations entered into the choice of this particular mode of procedure.

1. *The use of light elements as scatterers.*

In the atom of a light element the electron density is much less than in a heavy one. The phase relations between the beams scattered by the individual electrons will therefore be of much greater importance and the variation in scattering power be much more marked than in a heavier element. Again, the coefficient of absorption of light elements for X-rays is smaller, and thus the absorption effects will be, in general, less.

2. *The attempt to eliminate certain variables which it is impracticable to evaluate.*

Following the procedure of Hartree* we can write the intensity of the reflected beam as the product of two functions ϕ_1 and ϕ_2, where ϕ_1 contains easily evaluated variables and ϕ_2 those difficult or impossible to evaluate. The function ϕ_1 will contain the factor Z, the number of planes contributing to the reflexion; this is well known from crystallographic considerations. It contains the structure factor S, which is calculable from the known structure of aluminium. The doubt which enters into some crystal structure calculations, whether to use S itself or S^2 is of no account here, since every plane giving rise to a line has the same structure factor and this cancels out in the calculation of the relative F-values. Another well-known factor occurring in the function ϕ_1 is the polarization factor $\frac{1+\cos^2 2\theta}{2}$. The Lorentz factor is also contained in ϕ_1. This factor is dependent on the particular geometrical conditions of the experiment. It has been shown by Darwin † that the correct Lorentz factor for the Debye-Scherrer photograph is $\frac{1}{\sin^2\theta\cos\theta}$.

* Phil. Mag. l. p. 305 (1925).
† Phil. Mag. xliii. p. 800 (1922).

The factor ϕ_2 must be carefully considered, since it is this function which contains those variables which make intensity investigations so difficult. It contains the effect of heat motion of the atoms (the Debye temperature factor), the effects of extinction both primary and secondary, and finally the effect of absorption of the X-rays by the crystal material.

The Temperature Factor.—According to the recent calculations of Waller * this takes the form e^{-2M}, where M has the value $\tau \cdot \frac{4\pi^2}{\lambda^2} \cdot \sin^2\theta$.

Here τ is another temperature function characteristic of the material and is given by

$$\tau = \frac{3T \cdot N \cdot h^2}{4\pi^2 A \cdot x \cdot \Theta^2},$$

where T is the absolute temperature, N Loschmidt's number, h Planck's constant, x Boltzmann's constant, A the atomic weight and Θ the characteristic temperature of the material. Fortunately in the case of aluminium all these constants are known † and the expression can be evaluated. A simple calculation shows that, for the case of the Cu-radiation, this factor would multiply F_{224} by 1·001 if F_{111} is retained at unity. Hence the effect of this factor in these experiments is quite negligible. With the longer wave-length Fe-radiation this influence will be still less.

Primary and Secondary Extinction.—Primary extinction in reflexion from a crystal face may be looked upon as caused by the shielding action of the upper crystal layers of a crystalline fragment upon the lower layers. This effect is at a maximum in a perfect crystal and does not exist in an ideally imperfect crystal, nor in an irregularly orientated crystal powder where the crystal grains are sufficiently small. In these experiments a piece of aluminium wire of 0·06 cm. diameter was used. This wire, which originally showed a "Faserstruktur," was broken down into a mass of small crystals by heat treatment. In order to further enhance the homogeneity of the powder it was kept in rotation, about its own length as axis, during the whole exposure. Secondary extinction may be regarded as due to the shielding of the layers of one crystal particle upon those of another particle having the same orientation in the

* Dissertation, Upsala (1925).

† Laue & Mark, *Sitzber. d. preus. Akad. d. Wiss.* VI. p. 67 (1926).

mosaic crystal. This extinction is considered not to exist in the case of a powder photograph.

General Absorption in the Crystalline Mass.—It was at first hoped that the use of light elements, as well as having the advantage already pointed out, would make it unnecessary to apply any absorption correction. However, owing to the use of long wave-length X-rays, this result was not achieved and a correction had to be applied. It will be described in greater detail in a later section.

Experimental Procedure.

An ordinary Debye-Scherrer camera of diameter 5·72 cm. was used. It was fitted with a circular shield of lead ; the same camera was used in making all the photographs which are therefore comparable. The X-rays were obtained from a Hadding tube. The lines on the photographs were easily identified from a knowledge of the structure of aluminium.

Photometry.

The photometric records of the Debye-Scherrer films were made by the "Physikalische Reichsanstalt" of Berlin. One half of a complete film was used and was photometered along the central line of the film, *i. e.* in a direction at right angles to the Debye-Scherrer curves. A calibration wedge was prepared from the same photographic film, and was photometered along with each photograph under exactly the same conditions. The records showed the deflexion of an electrometer string caused by the difference between two photo-electric cells. The light falling on to one of these cells remained constant and that on the other varied by passing through the film to be photometered, which moved slowly across a very small slit in front of the second cell. The basic idea was that, with a constant X-ray beam, a line of intensity twice as great was obtained on a film if the time of exposure was doubled. The wedge was made by covering the film with a thick sheet of lead and then successively exposing it in strips of 1 cm. to the blackening action of the X-rays. The first step was exposed for 1 sec., the second for 2 secs., etc. The photometer record of the wedge therefore gives a means of converting an electrometer deflexion into a time (or intensity) value. In the same way, an electrometer deflexion on the record obtained from the Debye-Scherrer film could be changed into an intensity

value. The relationship between time and intensity is not true for very long exposures and dark lines where the silver salts of the film have been exhausted. In this region the calibration curve flattens off, the first portion being approximately a linear relationship between time (or intensity) and deflexion. Any peaks of the photometer record which came into this flat insensitive portion of the calibration curve were impossible to use. This photometry presupposes that the ratio between the intensity of two lines on a film is not altered by variations in the time of development, at least within the times of more or less normal development. A suitable Debye-Scherrer photograph had to be produced by varying the time of exposure until the reflexions required gave peaks of suitable intensity. This was the reason, already mentioned, why only the aluminium photographs were used in the final results. The record, showing the electrometer deflexion, was then converted into a curve, drawn out on graph paper, showing time (or intensity) ordinates. A general curve of the background of scattered radiation is drawn in and the area of the peaks superposed on this background can be estimated by means of the squared paper. The intensity of a line is proportional to the area of the corresponding peak.

Calculation of F.

The intensity of a line in a Debye-Scherrer photograph is given by

$$I = K \cdot S^2 \cdot F^2 \cdot Z \cdot \frac{1+\cos^2 2\theta}{2} \cdot \frac{1}{\sin^2\theta\cos\theta} \cdot e^{-2M}$$

where K is a proportionality factor. Neglecting the temperature factor and putting $K=1$, we get (in quite arbitrary units)

$$F^2 = \frac{2I\sin^2\theta\cos\theta}{S^2Z(1+\cos^2 2\theta)} \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

The angle functions for each line are easily calculated knowing the lattice dimensions of aluminium, $a=4{\cdot}05$ Å., and the wave-length of the X-rays.

Table I. gives the results of these calculations and measurements.

The figures are uncorrected for absorption and it is clear that this correction must be applied.

TABLE I.

Line.	Z.	Cu-photograph.			Fe-photograph.		
		θ.	I.	F^2.	θ.	I.	F^2.
111	8	19°3	13·2	0·1059	24°5	27·0	0·3700
200	6	22·4	9·1	0·1359	28·6	18·4	0·4770
220	12	32·6	9·6	0·1664	42·6	29·4	0·8225
113	24	39·3	15·4	0·1922	52·6	48·7	0·7300
222	8	*	*	*	56·1	16·8	0·7070
400	6	*	*	*	72·2	22·4	0·6250
133	24	56·3	9·6	0·1508			
240	24	58·6	9·6	0·1254			
224	24	69·3	17·8	0·1470			

* The resolving power of the camera, when Cu radiation was used, was too low to separate these two lines enough to prevent the corresponding peaks of the photometer record from overlapping. They were therefore not used in the calculation.

The Absorption Correction.

In the paper by Debye and Scherrer † intensity measurements were obtained from a powder-photograph and an absorption correction was applied, but no details of the method of correction were given. Prof. P. Debye, however, in a private communication informed me of the manner in which he carried out this correction, and I wish to express here my indebtedness to him for his help. The correction applied in this paper was made in a similar manner. An absorption correction, in a rather different form, has also been made by A. Claassen ‡.

Let the circle of fig. 1 represent the cross section of the rod of crystal powder, and let its centre be at C and its radius be a. Consider a ray which passes through the rod as far as the point X, where it strikes a crystal particle and is reflected at a glancing angle θ. The position of the point X can be fixed by means of two coordinates:—the angle ϕ and the radius vector $CX=r$. It can then be

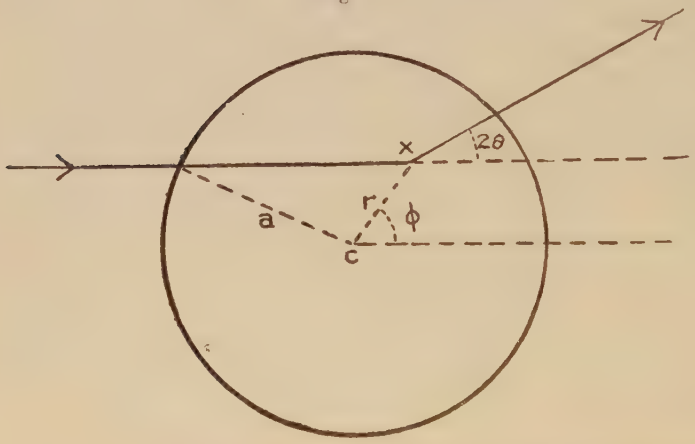
† *Loc. cit.*

‡ *Zeit. f. phys. Chem.* cxxiv. p. 139 (1926); Dissertation, Amsterdam (1926).

shown that the length of the path of the ray through the rod is given by

$$l = \sqrt{a^2 - r^2 \sin^2 \phi} + r \cos \phi + \sqrt{a^2 - r^2 \sin^2 (\phi - 2\theta)} - r \cos (\phi - 2\theta).$$

Fig. 1.



If now the absorption coefficient of the crystal powder is α, then the intensity is reduced by a factor A which is given by

$$A = \frac{\int_0^a \int_0^{2\pi} e^{-\alpha l} \cdot r \, dr \, d\phi}{\pi a^2}$$

where the integration is carried out over all the values of r and ϕ corresponding to all positions of the point X. It is impossible to evaluate this double integral; but it can, however, be solved by graphical integration, and although this method is very long and tedious, reliable values for A can be obtained. The radius of the rod of powder was 0·06 cm. and the mass absorption coefficients $\frac{\alpha}{\rho}$ of CuKα and FeKα rays in aluminium were taken as 50 and 100 respectively. For a fixed value of $\frac{r^2}{a^2}$ the values of the function $e^{-\alpha l}$ were calculated for a series of values of ϕ between 0 and 2π, the value of θ remaining constant, *i. e.* the calculation was being made for one line of the photograph. The first graphical integration then gave the value

of the integral $\int_0^{2\pi} e^{-a\iota} d\phi$ for a fixed value of $\frac{r^2}{a^2}$. This integral was evaluated for different values of $\frac{r^2}{a^2}$ ranging from 0 to 1, and a second integration then gave the value of the double integral. Putting this factor into formula (I.), we obtain

$$F^2 = \frac{2I \cdot \sin^2\theta \cos\theta}{A \cdot S^2 \cdot Z \cdot (1 + \cos^2 2\theta)}.$$

The values of F^2 in Table I. were now corrected by dividing by the appropriate A. The square root was taken and the value for F_{111} for both wave-lengths made unity. The results of these calculations are shown in Table II. Column 2 of this table gives the values of $\frac{\sin\theta}{\lambda}$.

Final Results and Remarks.

TABLE II.

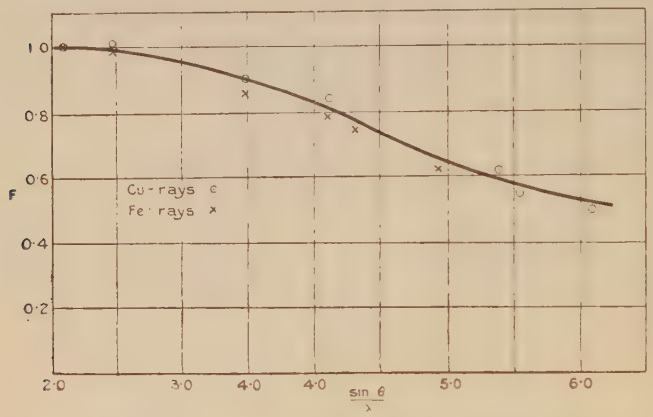
Line.	$\frac{\sin\theta}{\lambda}$.	Cu-photograph.		Fe-photograph.	
		A×10³.	F.	A×10³.	F.
111	2·15	18·0	1·000	12·5	1·000
200	2·48	22·0	1·010	16·5	0·993
220	3·50	35·0	0·900	30·25	0·961
113	4·11	44·5	0·340	39·5	0 790
222	4·29	*	*	42·25	0·753
400	4·92	*	*	52·5	0·636
133	5·40	65·5	0·627		
240	5·54	68·5	0·560		
224	6·09	80·0	0·517		

These results are also shown graphically in fig. 2. Here the F values are plotted against $\frac{\sin\theta}{\lambda}$. The crosses represent the values obtained by using Fe-radiation and the circles those obtained with Cu-radiation. A curve is drawn through all the points, as it is obviously impossible to draw separate curves for the Fe- and the Cu-points.

The conclusion to be drawn from these experiments is that, as far as the accuracy of the methods employed allows,

the scattering power F of an atom is a function of $\frac{\sin\theta}{\lambda}$ as demanded by theory.

Fig. 2.



It is of interest to consider the relative advantages and disadvantages of the photographic and ionization methods in the measurement of intensity. It would appear that, by using powdered crystals, the difficulties due to extinction, which occur when large crystals are used, can be avoided. But then, instead of simple and elegant measurements with the ionization chamber, we have the complicated process of photometry and further, the laborious and lengthy calculations for the absorption correction. The chief difficulty, and indeed a real danger, would seem to be the doubt about getting the powder particles sufficiently small and avoiding any preferential orientation, which would be fatal to intensity measurement, since certain lines would predominate. In view of the difficulties encountered in carrying out this work, the results are not published with any great claim to accuracy, but rather as a first attempt to investigate the variation of F with λ and also as a test of the reliability of photographic intensity measurements. Since the variation of F with λ is of great theoretical importance, an attempt by means of the ionization spectrometer to verify these results would be of the greatest value.

I take this opportunity of expressing my great indebtedness to the International Education Board for the grant of a Fellowship, which I held during the course of this work. I wish also to express my thanks to Dr. H. Mark, of the Kaiser Wilhelm Institut für Faserstoffchemie, Berlin, in whose laboratory the experiments were made, and to Prof. W. L. Bragg for their advice during the research.

XCIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 272.]

June 9th, 1926.—H. W. Monckton, Treas.L.S., Vice-President, in the Chair.

THE following communication was read :—

'A Contribution to the Geology of the Eastern Part of the Denbighshire Moors.' By Prof. P. G. H. Boswell, D.Sc., F.G.S.

The present paper is a first contribution to the revision of the geology of the Denbighshire moors. It deals with the eastern part of the area, about 72 square miles in extent, between Llanefydd, Denbigh, Ruthin, and the centre of the moors.

After describing the work of Sedgwick, Ramsay, and other former investigators in the area, the author gives a detailed account of the stratigraphical succession and faunal sequence, and comparison is made with the neighbouring areas of the Clwydian Range, the Llangollen area, and the district of Cautley and Ravenstonedale.

The greater part of the area consists of Upper Salopian strata, comprising rocks belonging to the zones of *Monograptus nilssoni*, *M. scanicus*, and *M. tumescens*, but the succession is much obscured by a thick mantle of Glacial Drift. For assistance in determining the sequence of the beds, the key to which is furnished by the graptolite fauna, the author is greatly indebted to Miss G. L. Elles, D.Sc.

Microscopic examination of the sediments has shown that they are all of shallow-water facies, varying from sandstones of medium grain to siltstones and mudstones which often contain bands of very fine material. Even in the latter, however, coarser grains of quartz occur sporadically. On the whole, the deposits increase in coarseness as they become younger, and this is attributed to the filling-up and shallowing of the geosyncline; while minor alterations in the grade-characters are attributed to current action, although they may be the result of slight oscillatory earth-movements.

The rhythmical banding of the Nantglyn Flags suggests periodicity, possibly seasonal in character.

Tectonically, the area constitutes the north-eastern part of the syncline of the Denbighshire moors, pitching north-eastwards. It is, moreover, intensely faulted, and nowhere is a continuous sequence of the zones visible. The dominant faults are of north- and south trend, but swing north-north-westwards in the northern part of the area, and apparently south-south-westwards south of

the district. The structure is interpreted as the result of successive upthrows towards the west, but some lateral movement is probable.

Numerous cross-faults, usually antedating the north-and-south faults, carve the country into blocks.

While much of the faulting is of pre-Carboniferous age and related to the folding, movement on the north-and-south faults was, at least in part, renewed in post-Carboniferous times.

The rocks in the central part of the area have been subjected to intense crushing and shearing.

Cleavage is general throughout the district, and is related in direction to the Caledonian folding.

December 1st.—Dr. F. A. Bather, M.A., F.R.S., President, in the Chair.

The following communication was read:—

'The Geology of the Snowdon Massif (North Wales).' By Howel Williams, M.A., M.Sc., D.I.C., F.G.S.

The area described is limited on the north-east by the Pass of Llanberis, on the south-east by the Vale of Gwynant, on the south-west by the Colwyn and Gwyrfai Valleys to near the village of Salem, and on the north-west by the supposed line of junction between the Cambrian and the Ordovician rocks.

The general stratigraphical succession is as follows:—

			Thickness in feet.
Lower Caradoc.	Snowdon Volcanic Rocks.	Upper Rhyolitic Series. Potash-rhyolites and tuffs	200–300
		Bedded Pyroclastic Series. Basic pumice-tuffs, with interbedded potash-rhyolites and fossiliferous sediments	500–1200
		Lower Rhyolitic Series.	
		(*d*) Unstratified, potash-rhyolite-tuffs	600–1500
		(*c*) Flinty rhyolites	Up to 400
		(*b*) Pitt's Head banded rhyolites	150–200
		(*a*) Nodular rhyolites	5–20
		Gwastadnant Grits. Banded tufaceous grits, with thin flows of potash-rhyolite	400–1200
Lower Llandeilo.		Glanrafon Slates. Silky, usually banded, blue-grey slates, with flows of soda-rhyolite and keratophyre (Talgau Lavas). Zones of *Nemagraptus gracilis* and *Glyptograptus teretiusculus* are distinguished.	700–1100
Llanvirn.		Maesgwm Slates. Blue-black, micaceous, unbanded slates, with thin grit-courses. Zones of *Didymograptus bifidus* and *D. murchisoni*.	1500–1700
Arenig.		Plas-y-Nant Beds. Grey and grey-green, striped slates, with bands of quartzose grit. The basal grits are extensively tourmalinized	900–1500
		Unconformity.	
Upper Cambrian.		Ffestiniog Beds. Maentwrog Slates. Bronllwyd Grits.	

The exact relationship between the Ordovician and the Cambrian Systems on the northern flank of Snowdon is uncertain. The Ffestiniog Beds exposed on Moel Eilio are overlain, with only a very slight discordance of dip, by a group of tourmalinized sediments, tentatively regarded as the basal Arenig Grits. Above these grits is a thick series of grey and grey-green, apparently unfossiliferous, slates that bear a lithological resemblance to certain shales immediately above the basal Ordovician grit in the Nantlle Valley and to the lowest Arenig rocks of Llanfrothen, Portmadoc.

The Llanvirn Beds are more than twice as thick as their equivalents in Anglesey, although only the top 400 or 500 feet are referable to the zone of *Didymograptus murchisoni*. The highest graptolitiferous horizon recognized on Snowdon is in the lower part of the zone of *Nemagraptus gracilis* (Llandeilo) and lies almost immediately beneath the earliest volcanic rocks on the mountain, the Talgau Lavas. It is separated from the Snowdon Volcanic Suite proper by a thick and persistent group of banded grits, carrying lava-flows that may perhaps belong to the same volcanic suite as the lavas of Capel Curig and Y Glyder Fach.

Ramsay's threefold division of the Snowdon Volcanic Suite remains the most useful basis for its study. The Upper and Lower Rhyolitic Series were derived from a potash-rich magma, not unlike that which furnished the 'granitic' intrusions of Moel Perfedd, Bwlch-y-Cywion, and Mynydd Mawr. Support is thus lent to the view, expressed by Dr. A. Harker, that these intrusions may represent the sites of old volcanoes from which many of the Caernarvonshire lavas were erupted. The Bedded Pyroclastic Series is typically composed of green, well-banded pumice-tuffs of andesitic to basaltic character, and carries abundant bombs and lapilli of spilite and keratophyre. About Snowdon summit and elsewhere that series includes fossiliferous sediments of Lower Caradocian age, and is interbedded with potash-rhyolites and tuffs. The approximate age of the Snowdon Volcanic Suite is inferred to be between Middle Llandeilian (Zone of *Climacograptus peltifer*) and Middle Caradocian (Zone of *Dicranograptus clingani*).

Many dykes, inclined sheets, and bosses of quartz-porphyry, microgranophyre, and intrusive rhyolite occur on Snowdon, the greatest intrusion being that of Crib Goch, formerly considered to be an outlier of the Upper Rhyolitic Series. Both mineralogically and chemically, the acid intrusive rocks resemble the Snowdon rhyolites.

Pre-cleavage sills of augite-dolerite and spilitic dolerite occur at several horizons, and present various biotite- and copper-rich modifications. Where they have been subjected to intense pressure, the dolerites have yielded such metamorphic differentiates as amphibolite and epidosite. A sill of decomposed quartz-dolerite is intrusive among the Llanvirn slates near Quellyn Lake.

The major folding is of north-east-and-south-west strike, and occurred almost wholly after the period of basic intrusions. Its

dominant expression is the so-called 'Snowdon Syncline,' the north-western limb of which lies in a recumbent position in the area immediately south of Rhyd-ddu. The major folding was succeeded first by a cleavage of similar strike, and subsequently by a minor folding and thrusting due to pressures directed south-eastwards; the thrusting being most pronounced along the recumbent limb of the 'Snowdon Syncline.' Finally, the area was broken into blocks by faults, most of which belong to the same family of movements as those just enumerated, although some may have moved again during the Tertiary Era.

January 5th, 1927.—Dr. F. A. Bather, M.A., F.R.S., President, in the Chair.

The following communication was read:—

'The Nature and Origin of Soil-Polygons in Spitsbergen.' By Charles S. Elton (communicated by Dr. J. A. Douglas, M.A., Sec.G.S.).

Observations and excavations in the north of Spitsbergen have made it necessary to revise the classification of the various types of soil-polygons found in that country. New suggestions are also made as to the way in which they are formed. Polygonal soils are divided primarily into mud-polygons and stone-polygons. The mud-polygons are formed in two quite different ways: there are larger ones produced by frost-expansion of the soil in winter, and smaller ones formed by drying of the soil in summer. In the latter season both are usually found combined together. Stone-polygons are more difficult to explain, and there are probably several factors at work. A new factor is described in this paper, which acts in the following way:—mixed materials, consisting of rocks, gravel, and mud, become differentially arranged in a vertical direction, so that there is mud below, grading into stones on the surface. The mud freezes in winter, expands, and forms regular mud-polygons, invisible from the surface at that stage. Later, as the overlying stones become disintegrated, the centres of the mud-polygons reach the surface, and when they freeze in winter exert a lateral pressure forcing the stones outwards, forming at first, rings, and later, stone networks. This explanation of the origin of stone-polygons is confirmed by a series of excavations of various stages in the process, beginning with weathering rock-detritus, and ending with stone-polygons.

Finally, evidence is given of the importance of plants in stabilizing the surface-soil in Arctic regions.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

MAY 1927.

XCIV. *The Viscosity of a Gas composed of Sutherland Molecules of a Particular Type.* By H. R. Hassé, *M.A. D.Sc., and* W. R. Cook, *B.Sc.**

THE particular model of a gaseous molecule introduced by Sutherland has played a very important part in the development of the kinetic theory of gases. According to this model the molecule behaves as a rigid elastic sphere of definite radius s_0, but is, in addition, the source of an attractive force of a spherically symmetrical type, and Sutherland showed on the basis of the older type of kinetic theory involving the idea of a mean free path that the viscosity η of a gas composed of such molecules would vary with the absolute temperature T according to the law

$$T^{\frac{1}{2}}\Big/\left(1+\frac{S}{T}\right),$$

where S is a constant depending on the attractive force. This law was found to be in accordance with experiments in a very large number of cases, only the light gases, helium and hydrogen, proving an exception.

Theoretical developments associated with the names of Chapman and Enskog have shown that the above formula for the variation of viscosity with temperature is approximate, and only applicable when S/T is small, in which case the dependence of S on the actual law of attractive

* Communicated by the Authors.

force has been given by James and Enskog for certain types of force.

Recent investigations by Lennard-Jones have made it clear that any model involving a rigid sphere is quite unsuitable for the representation of physical phenomena, and that the repulsive property associated with a concentrated effect at a definite distance s_0 from the centre of the molecule must be replaced by a repulsive force varying with the distance from that centre.

Nevertheless it is of interest to see how Sutherland's model will work in a particular case in which the theoretical formula can be worked out accurately, and not merely approximately, and to compare the results obtained by comparison with experiments on the variation of viscosity with temperature with those obtained from experiments on the isotherms of gases.

The particular case which can be so treated is that in which the attractive force varies as the inverse fifth power of the distance r from the centre of a molecule, the problem being to obtain the values of the diameter $\sigma\,(=2\,s_0)$, and of the attractive force constant μ from comparison with the experimental data. The value of the integral occurring in the theoretical formula can be derived from calculations carried out by one of the authors in another connexion *, which calculations are the basis of those given in this paper †.

1. *The Formula for the Viscosity of the Gas.*

The formula for the coefficient of viscosity η of a gas is given by Chapman ‡ in the form

$$\eta = \frac{5m}{4h^3m^3}\left(\frac{2\pi}{hm}\right)^{\frac{3}{4}}\frac{1}{\pi \mathrm{R}_{11}'}(1+\epsilon),$$

where $h=(2\mathrm{RT})^{-1}$, R being the gas constant, and R_{11}' is defined by

$$\mathrm{R}_{11}' = 4\pi\int_0^\infty \mathrm{V}^7 e^{-\frac{hm}{2}\mathrm{V}^2}\,d\mathrm{V}\int_0^\infty \sin^2\theta\cos^2\theta\, p\,dp,$$

where V is the relative velocity of any two molecules before

* H. R. Hassé, Phil. Mag. vol. i. p. 139 (1926).

† [This application of the former calculations to the problem of viscosity was suggested by Dr. Lennard-Jones, and the present paper was planned as a joint investigation. Owing to pressure of other work, his part in the present paper has been taken over by Mr. W. R. Cook.—H. R. H.]

‡ Chapman, Phil. Trans. A, vol. ccxvi. p. 279 (1915).

an encounter, $\pi - 2\theta$ is the angle through which the relative path is deflected by the encounter, and p is the length of the perpendicular from the centre of either molecule in the direction of V. The factor $(1+\epsilon)$ can be taken as unity, its greatest value being 1·016 in the case where the molecules behave simply as elastic spheres. In the case of weak attractive forces, when the Sutherland formula is applicable, Chapman has shown that ϵ has a value of about 1·004 for ordinary gases, so that we may expect its value to be still nearer to unity when the attractive forces play a more important part, as is the case here. The value of θ is to be obtained from the dynamics of an encounter in which the attractive force at a distance r is μr^{-5}. If m is the mass of a molecule of the gas, the differential equation for $dr/d\theta$ is given by

$$\frac{1}{r^2}\left(\frac{dr}{d\theta}\right)^2 + 1 = \frac{r^2}{p^2} + \frac{4r^2}{mp^2\mathrm{V}^2}\frac{\mu}{4r^4},$$

or, putting $\zeta = p/r$,

$$\left(\frac{d\zeta}{d\theta}\right)^2 + \zeta^2 = 1 + \frac{\mu\zeta^4}{mp^4\mathrm{V}^2}.$$

If $\zeta = (2\beta^2)^{\frac{1}{2}}x$, and $4\beta^4\mu = mp^4\mathrm{V}^2$, this equation reduces to

$$2\beta^2\left(\frac{dx}{d\theta}\right)^2 = 1 - 2\beta^2x^2 + x^4,$$

whence

$$\theta = (2\beta^2)^{\frac{1}{2}}\int_0^{x_1}\frac{dx}{(1-2\beta^2x^2+x^4)^{\frac{1}{2}}}, \quad . \quad . \quad . \quad (1)$$

where x_1 is defined below.

If we put

$$\tfrac{1}{2}hm\mathrm{V}^2 = z^2, \quad \text{and} \quad p^2 = \frac{2\beta^2}{\mathrm{V}}\left(\frac{\mu}{m}\right)^{\frac{1}{2}} = \frac{\beta^2}{z}(2h\mu)^{\frac{1}{2}},$$

then

$$\mathrm{R}_{11}' = (2h\mu)^{\frac{1}{2}}\left(\frac{2}{hm}\right)^4\int_0^\infty z^6e^{-z^2}\,dz\int_0^\infty 2\pi\sin^2\theta\cos^2\theta\,d(\beta^2),$$

and the coefficient of viscosity η is equal to

$$\frac{5m}{64}\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\left(\frac{2\mathrm{RT}}{m}\right)^{\frac{1}{2}}\left(\frac{\mathrm{RT}}{\mu}\right)^{\frac{1}{2}}\frac{1}{\mathrm{X}} \quad . \quad . \quad . \quad . \quad (2)$$

where

$$\mathrm{X} \equiv \int_0^\infty z^6e^{-z^2}\,dz\int_0^\infty \sin^2\theta\cos^2\theta\,d(\beta^2). \quad . \quad . \quad (3)$$

The calculation of θ from (1) depends on the relative effect of the attractive forces and the elastic collisions. Using the same notation as that given in the paper referred to *, we introduce a symbol λ, given by

$$\lambda^2 = \mathrm{RT}\,4\sigma^4/\mu, \quad \text{or} \quad \mathrm{RT}/\mu = \lambda^2/4\sigma^4,$$

where σ is the distance between the centres of two molecules at the instant of collision. The upper limit x_1 of the integral in (1) is then the least root of the denominator, if it exists, and is less than $(\lambda z)^{-\frac{1}{2}}$, and x_1 is equal to $(\lambda z)^{-\frac{1}{2}}$ if this is not the case. Reference may be made to the paper for the details of the calculation of θ as a function of λz by means of elliptic integrals, to which (1) can be reduced in all cases.

When the elastic collisions are the determining factor, $\mathrm{X} \to \frac{1}{4}\lambda$, so that from (2) η tends to the value

$$\frac{5}{64}\left(\frac{m\,\mathrm{RT}}{\pi}\right)^{\frac{1}{2}}\frac{4}{\sigma^2} = \frac{5}{64}\left(\frac{m\,\mathrm{RT}}{\pi}\right)^{\frac{1}{2}}\frac{1}{s^2},$$

where s is the radius of the molecule, in agreement with the usual result (*cf.* Jeans, 'Dynamical Theory of Gases,' 3rd edition, p. 276).

2. *Calculation of* X *as a Function of* λ.

This follows the lines given in the previous paper. The quantity X is given by

$$\mathrm{X} \equiv \int_0^\infty x\, z^6 e^{-z^2}\, dz, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$x \equiv \int_0^{\beta} \cos^2\theta \sin^2\theta\, d(\beta^2). \quad . \quad . \quad (5)$$

Owing to the fact that $\sin^2\theta\cos^2\theta$ takes the place of $\cos^2\theta$ in the integrand of the corresponding function of $z\lambda$, it was found necessary in almost all cases to double the number of intervals in the numerical integration, which resulted in a great increase in the arithmetical work involved.

As before, the value of x has to be calculated separately for $\beta > 1$ and $\beta < 1$, and, further, for values of $z\lambda$ greater and less than 1.

* H. R. Hassé, *loc. cit.* p. 141.

For $z\lambda \leq 1$ these are given in the following table :—

TABLE I.

$z\lambda \rightarrow$	0	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{3}{4}$	1
$x(\beta<1)$	·12739	·12831	·12885	·12990	·13063	·13218	·13483	·13776
$x(\beta>1)$	·06518	·06518	·06518	·06518	·06518	·06518	·06518	·06518
x	·19257	·19349	·19403	·19508	·19581	·19736	·20001	·20294

Owing to the existence of a maximum followed by a minimum in the range $1<z\lambda<2$, the values of x for points in this range are given in a separate table, in which some of the values of $z\lambda$ have been chosen for convenience in calculation, and the values of x for $z\lambda>2$ are given in the following table :—

TABLE II.

$z\lambda \rightarrow$	1	1·07232...	1·15470...	1·23346...	$1\frac{1}{3}$	1·47160...	$1\frac{2}{3}$	2
$x(\beta<1)$	·13776	·13895	·13854	·13797	·14035	·14842	·16238	·18006
$x(\beta>1)$	·06518	·06490	·06693	·06786	·06450	·05491	·04154	·03321
x	·20294	·20385	·20547	·20583	·20485	·20333	·20392	·21327

TABLE III.

$z\lambda \rightarrow$	2	3	4	6	8
$x(\beta<1)$	·18006	·18434	·16546	·12905	·10388
$x(\beta>1)$	·03321	·08891	·18307	·37998	·56927
x	·21327	·27325	·34853	·50903	·67315

In order to carry out the calculation of X from (4), it is most convenient to express the results of Tables I., II., and III. in the form of algebraic functions of $z\lambda$, and then to use Gamma functions for the integration. Writing t for $z\lambda$, the following expressions were obtained for various ranges of values of t :—

$$(0 \leq t \leq \tfrac{1}{4}), \quad x = \cdot19257 + \cdot00371\, t^{\frac{1}{2}} + \cdot00504\, t^{\frac{3}{2}},$$

$$(\tfrac{1}{4} \leq t \leq 1), \quad x = \cdot19312 + \cdot00721\, t + \cdot00262\, t^{2},$$

$$(1 \leq t \leq 2), \quad x = \cdot03225 + \cdot38104\, t - \cdot27544\, t^{2} + \cdot06510\, t^{3},$$

$$(2 \leq t < \infty), \quad x = \tfrac{1}{12}\, t + \cdot05073\, t^{-1} + \cdot16965\, t^{-3}.$$

The approximation $\frac{1}{1\cdot 2}t$ corresponding to the case of elastic collisions is a useful check on the values of x for large values of t.

The values of X were then calculated for values of λ at intervals of 0·05 up to $\lambda=1$, and at intervals of 0·1 from $\lambda=1$ to $\lambda=4$, and are given in Table IV. It will be noticed that as λ increases, X tends to the correct limiting value $\frac{1}{4}\lambda$.

The errors in the calculation of X arise from those in x due to replacing the tabulated values by the approximate algebraic expressions given above. The latter errors are estimated to be less than 1 in 1900 for the first range of values of t above, less than 1 in 4000 for the second range, less than 1 in 300 for the third range, and less than 1 in 3000 for the range $2<t<\infty$. The inadequacy of the approximation in the range $1<t<2$ arises from the existence of maximum and minimum values in this range, and the error in the final calculation of X is largely due to the difficulty of getting a satisfactory approximation in this range. The consequent errors in X can be calculated, and are less than 0·0004 when $0<\lambda<0\cdot5$, are less than 0·001 when $0\cdot5<\lambda<1\cdot2$, and then diminish steadily as λ increases, being less than 0·0004 for all values of $\lambda>1\cdot2$.

Table IV.

λ.	X.	X (smoothed).	λ.	X.	λ.	X.
0·0	·3200	·3200	1·0	·3557	3·0	·7700
·05	·3221	·3221	1·1	·3666	3·1	·7941
·10	·3233	·3233	1·2	·3799	3·2	·8184
·15	·3245	·3243	1·3	·3952	3·3	·8427
·20	·3258	·3254	1·4	·4122	3·4	·8670
·25	·3272	·3263	1·5	·4306	3·5	·8914
·30	·3314	·3273	1·6	·4501	3·6	·9159
·35	·3304	·3282	1·7	·4704	3·7	·9404
·40	·3320	·3292	1·8	·4915	3·8	·9649
·45	·3336	·3302	1·9	·5132	3·9	·9894
·50	·3351	·3313	2·0	·5353	4·0	1·0140
·55	·3364	·3325	2·1	·5578		
·60	·3374	·3338	2·2	·5807		
·65	·3383	·3352	2·3	·6038		
·70	·3393	·3369	2·4	·6271		
·75	·3405	·3389	2·5	·6506		
·80	·3422	·3413	2·6	·6742		
·85	·3446	·3441	2·7	·6980		
·90	·3476	·3472	2·8	·7219		
·95	·3512	·3510	2·9	·7459		

It will be noticed that the existence of a maximum and minimum in x, referred to above, persists in the value of X.

This may possibly be due to the particular molecular model chosen. For the purpose of comparison with experiment the value of X was smoothed in the range $0<\lambda<1$, the maximum change introduced by this process being 0·004 at $\lambda=0{\cdot}55$, which is more than the estimated maximum error in the calculation. It will be found, however, that, in the comparison with experiment, the values of λ concerned only come as low as 0·5 at the lowest temperatures considered. Sutherland's formula, applicable only to weak attractive forces varying inversely as the fifth power of the distance, gives in our notation *

$$X=\tfrac{1}{4}\lambda(1+0{\cdot}1956\,\lambda^{-2}). \quad . \quad . \quad . \quad . \quad (6)$$

If we compare this with the accurate value for X, we find that for $\lambda=4$, $X=1{\cdot}0122$ from (6), as compared with the accurate value 1·0140 ; $X=\cdot7663$ for $\lambda=3$, as compared with ·7700 ; and $X=\cdot5245$ for $\lambda=2$, compared with ·5353, so that in this case Sutherland's formula is in error by 2 per cent. For $\lambda=1$, (6) gives ·2989, while the accurate value is ·3557, and the error becomes larger still for lower values of λ.

3. *Determination of the Force Constant and Diameter by comparison with Experiment.*

Equation (2) for η may be written

$$\eta=\frac{5}{64}\left(\frac{Rm}{\pi}\right)^{\frac{1}{2}}T\,\frac{f(\lambda)}{\sigma^2},$$

where

$f(\lambda)\equiv\lambda/X$, and we have used the relation $\mu(RT)^{-1}=4\sigma^4\lambda^{-2}$,

or
$$\log(\eta T^{-\frac{1}{2}})=\log f(\lambda)+\log p, \quad . \quad . \quad . \quad (7)$$

where
$$p=\frac{5}{64\sigma^2}\left(\frac{Rm}{\pi}\right)^{\frac{1}{2}}.$$

Again, since $\lambda^2\mu=4R\sigma^4T$,

we have
$$\log\lambda=\tfrac{1}{2}\log T+\tfrac{1}{2}\log(4R\sigma^4/\mu). \quad . \quad . \quad . \quad (8)$$

The experiments on the variation of viscosity with temperature will give $\eta T^{-\frac{1}{2}}$ as a function of T, and the theory gives $f(\lambda)$ as a function of λ. If therefore $(\log\eta T^{-\frac{1}{2}})$ is plotted against $\log T$ on transparent paper, and $\log f(\lambda)$ is plotted against $\log\lambda$, the scales being so chosen that the scale of $\log(\eta T^{-\frac{1}{2}})$ is the same as that of $\log f(\lambda)$, and the

* James, Proc. Camb. Phil. Soc. vol. xx. p. 447 (1921).

scale of $\log\lambda$ is equal to that of $\frac{1}{2}\log T$, and the curves can be made to fit by a parallel transformation *, we shall have

$$\log(\eta T^{-\frac{1}{2}}) - \log f(\lambda) = Q, \quad \tfrac{1}{2}\log T - \log\lambda = P. \quad . \quad (9)$$

It follows then from (7) and (8) that

$$\log p = Q \quad \text{and} \quad \tfrac{1}{2}\log(4R\sigma^4/\mu) + P = 0,$$

whence

$$\left.\begin{aligned} \log\sigma^2 &= \log\left(\frac{5}{64}\frac{R}{\sqrt{\pi}}\right) + \tfrac{1}{2}\log\left(\frac{m}{R}\right) - Q \\ \text{and} \quad \log\mu &= \log 4R + 4\log\sigma + 2P, \end{aligned}\right\} . \quad (10)$$

from which σ and μ are determined.

The success of the method depends on the superposition of the two curves, and it is clear that there are other methods of using the theoretical formula for comparison with experiment. All methods should of course give the same results, so that the errors which may arise in the use of any method involving the superposition of two curves are indicated by applying two different methods of using the theoretical formula for comparison with experiment. Different methods amount to the addition or subtraction of multiples of $\log\lambda$, and the choice depends on the suitability of the resulting curves for the purpose of fitting one on to the other by a parallel transformation. For example, we may write

$$\eta T^{-\frac{3}{2}} = \frac{5\sigma^2 R}{16\mu}\left(\frac{mR}{\pi}\right)^{\frac{1}{2}} \frac{f(\lambda)}{\lambda^2},$$

whence

$$\log(\eta T^{-\frac{3}{2}}) - \log(f(\lambda)/\lambda^2) = \log q,$$

where

$$q = \frac{5\sigma^2 R}{16\mu}\left(\frac{mR}{\pi}\right)^{\frac{1}{2}}.$$

The parallel transformation then gives

$$\log(\eta T^{-\frac{3}{2}}) - \log(\lambda^{-2} f(\lambda)) = Q', \quad \tfrac{1}{2}\log T - \log\lambda = P',$$

so that

$$\log\left\{\frac{5\sigma^2 R}{16\mu}\left(\frac{mR}{\pi}\right)^{\frac{1}{2}}\right\} = Q', \quad \tfrac{1}{2}\log\left(\frac{4R\sigma^4}{\mu}\right) + P' = 0,$$

whence it follows that

$$\left.\begin{aligned} 2\log\sigma + 2P' + Q' + \log\left\{\frac{5}{64}\left(\frac{mR}{\pi}\right)^{\frac{1}{2}}\right\} &= 0, \\ \log\mu = 4\log\sigma + 2P' + \log 4R. \end{aligned}\right\} . \quad . \quad (11)$$

* This method, originally due to Keesom, has been used by Lennard-Jones for a similar investigation in connexion with the equation of state of a gas.

The superposition of the two curves can never be exact, so that an approximate fit can be obtained for several pairs of values of the constants P, Q of the transformation. For each of these approximate fits the value of $\Sigma(s^2)$ is calculated, where s is the perpendicular distance from the experimental points to the theoretical curve, and the minimum value of $\Sigma(s^2)$ is then taken to give the best fit. In all cases the unit of measurement for these lengths was ·01 inch.

Sutherland's approximate formula gives from (2) and (6)

$$\eta T^{-\frac{3}{2}} = \frac{5\sigma^2 R \left(\frac{mR}{\pi}\right)^{\frac{1}{2}}}{16\mu \frac{1}{4}\lambda^2(1+0{\cdot}1956\lambda^{-2})},$$

or

$$\frac{T^{\frac{3}{2}}}{\eta} = \frac{4\mu}{5\sigma^2 R}\left(\frac{\pi}{mR}\right)^{\frac{1}{2}}\left(0{\cdot}1956 + \frac{4R\sigma^4}{\mu}T\right), \quad . \quad (12)$$

giving $T^{\frac{3}{2}}\eta^{-1}$ as a linear function of T. From the values of the constants in this linear function found by comparison with experiment the values of σ and μ can be determined, and can be compared with the values obtained when the accurate formula is used.

4. *Results of Comparison with Experiment.*

The actual working out of the application to a particular gas may be illustrated in detail by taking the case of argon, the viscosity of which has been measured by Schmidt * for a range of temperatures from 90° abs. to 456° abs. These results, together with the values of $\log(\mu T^{-\frac{1}{2}})$ and $\log T$, form the data for drawing the experimental curve, and are given in Table V.

TABLE V.—Viscosity of Argon.

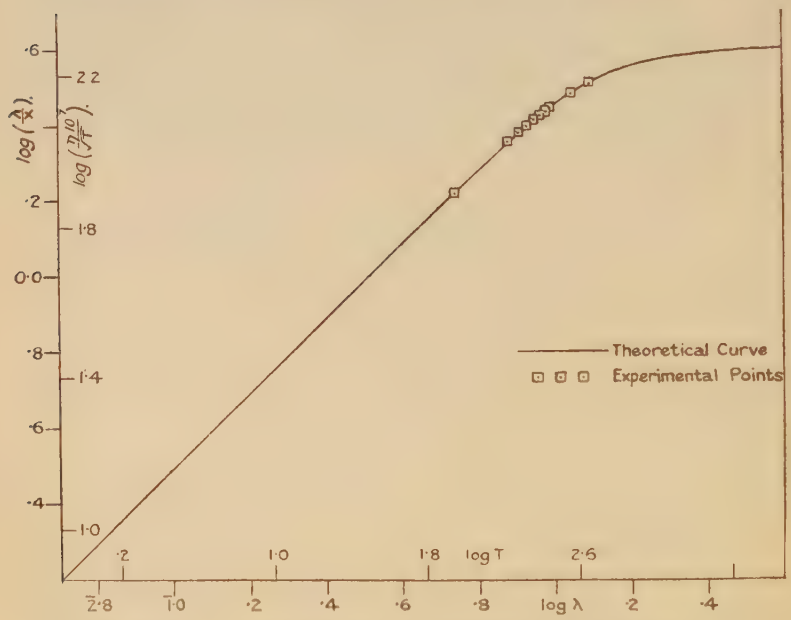
T (abs.).	$\eta\, 10^7$.	log T.	$\log\left(\frac{\eta\, 10^7}{\sqrt{T}}\right)$.
456·4	3243	2·6593	2·1813
372·8	2751	2·5715	2·1538
286·3	2207	2·4568	2·1154
272·9	2116	2·4360	2·1075
252·8	1987	2·4028	2·0968
232·9	1854	2·3672	2·0845
212·9	1697	2·3282	2·0656
194·3	1575	2·2885	2·0530
168·7	1379	2·2271	2·0260
89·9	735·6	1·9538	1·8898

* Schmidt, *Ann. d. Phys.* vol. xxx. p. 400 (1909).

Table VI. contains the values of P and Q giving the best fit, the extreme values of P and Q for which the curves may be said to fit, together with the corresponding values of the diameter σ, the force constant μ, and $\Sigma(s^2)$.

TABLE VI.—Results for Argon.

P.	Q.	$\sigma 10^8$.	$\mu 10^{13}$.	$\Sigma(s^2)$.
1·258	$\bar{6}$·691	2·922	1·314	93
1·237	$\bar{6}$·674	2·978	1·287	42
1·206	$\bar{6}$·651	3·060	1·243	92



Superposition of theoretical curve and the experimental curve for Argon.

The superposition of the theoretical and experimental curves in the case of the best fit is given in the figure, and the results are expressed in tabular form in the next table, together with those given by using Sutherland's formula, in which the constants have been recalculated by the method of least squares giving the value of S as 147·8.

TABLE VII.—Observed and Calculated Viscosity of Argon.

T (abs.).	$\mu 10^7$ (obs.).	$\mu 10^7$ (calc.).	$\mu 10^7$ (Sutherland).
456·4	3243	3242	3212
372·8	2751	2767	2752
286·3	2207	2217	2221
272·9	2116	2127	2133
252·8	1987	1987	1997
232·9	1854	1844	1858
212·9	1697	1697	1714
194·3	1575	1559	1576
168·7	1379	1364	1378
89·9	735·6	741·1	7·4

The other gases considered were nitrogen *, carbon-dioxide †, and air †, and the results are given in Table VIII., only the values for the best fit being given in each case.

TABLE VIII.—Results for N_2, CO_2, and Air.

Gas.	P.	Q.	$\sigma 10^8$.	$\mu 10^{43}$.	$\Sigma(s^2)$.
N_2	1·1525	$\bar{6}$·514	3·278	1·275	26
CO_2	1·2957	$\bar{6}$·543	3·550	3·405	77
Air.....	1·167	$\bar{6}$·538	3·216	1·267	23

In order to test the accuracy of this method of superposition of the experimental and theoretical curves, the values of $\log(\eta T^{-\frac{3}{2}})$ were calculated in the case of, air, and equations (11) were employed to find the values of σ and μ, with the result that $P'=1{\cdot}1577$, $Q'=\bar{1}{\cdot}2205$, $\sigma 10^8=3{\cdot}224$, and $\mu 10^{43}=1{\cdot}226$. These results show an excellent agreement with those given in Table VIII. for the diameter σ, the values for which differ by less than

* Schmidt, *Ann. d. Phys.* vol. xxx. p. 398 (1900). Vogel, *Ann. d. Phys.* vol. xliii. p. 1258 (1914). Kia Lok Yen, Phil. Mag. vol. xxxviii. p. 582 (1919).

† Breitenbach, *Ann. d. Phys.* vol. v. p. 166 (1914). Vogel, *loc. cit.*

1 in 300, but show that the values of μ cannot be relied upon to an accuracy of more than 4 per cent.

The case of water-vapour is of some interest, as it gives a very high value (767) for Sutherland's constant S, so that S/T is certainly not small. Unfortunately, its viscosity has only been measured at four temperatures covering a very small range*. For this reason it is not possible to obtain results of any great value, as is evident from the fact that the extreme values of P and Q differ very much from those taken for the best fit, and is also shown by the larger values of $\Sigma(s^2)$, and by the wide divergence in the values of σ.

Table IX.—Results for Water-Vapour.

P.	Q.	$\sigma 10^8$.	$\mu 10^{43}$.	$\Sigma(s^2)$.
1·488	$\bar{6}$·558	2·790	3·147	210
2·045	$\bar{5}$·698	1·517	3·402	140
2·382	$\bar{5}$·429	1·024	3·491	210

It is of interest to see what part of the theoretical curve for X as a function of λ is used in the comparison with experiment. In the case of argon λ ranges from ·50 to 1·2, in the case of nitrogen and air from ·60 to 1·5, and for carbon dioxide from ·65 to 1·2. The range of values is in all cases quite outside that in which Sutherland's approximate formula would hold. This formula was applied to these gases, the Sutherland constant being re-determined in view of the additional experimental results, and the

Table X.

Gas.	S.	$\sigma 10^8$ (1).	$\mu 10^{43}$ (1).	$\sigma 10^8$ (2).	$\mu 10^{43}$ (2).
Argon	147·8	2·90	2·944	2·98	1·287
Nitrogen	107·4	3·15	2·961	3·28	1·275
Carbon dioxide...	228·8	3·36	8·172	3·55	3·405
Air	112	3·10	2·881	3·22	1·267

(1) From Sutherland's formula. (2) From the accurate formula.

* Smith, Proc. Roy. Soc. vol. cvi. p. 93 (1924).

values of σ and μ are given in Table X. for comparison with the values obtained above by using the accurate formula.

The table shows that, while the values of the diameter σ do not differ very much, there is a very considerable difference in the values of the force constant μ as given by the two formulæ, the accurate values being very much lower than those determined from Sutherland's formula. The difference between the two sets of results increases as the value of the Sutherland constant S increases, as we should expect.

That the agreement between theory and experiment on the basis of the approximate formula of Sutherland may be quite as good as that obtained on the basis of the accurate formula, is shown in the case of Argon by Table VII., and also by Table XI., which refers to air.

TABLE XI.—Viscosity of Air.

T.	$\eta\,10^6$ (obs.).	$\eta\,10^6$ (calc.) (1).	$\eta\,10^6$ (calc.) (2).
575	299	296	296
455·5	256	254	253
372·2	220	220	219
288·1	181	182	181
273·1	173	174	173
251·7	164	163	162
194·6	132	130	131
81·6	57·4	57·1	56·8

(1) From the accurate formula. (2) From Sutherland's formula.

This affords a striking example of the fact that agreement between a theoretical formula and experiment can by no means be taken as a justification of the accuracy of the formula.

It is more interesting to compare the results obtained in this paper, which are deduced from the variation of viscosity with temperature, with those obtained for argon * and nitrogen † from the equation of state, since the methods of

* J. E. Lennard-Jones, Proc. Roy. Soc. A, vol. cvi. p. 463 (1924).
† J. E. Lennard-Jones and W. R. Cook, Proc. Roy. Soc. A, vol. cxii. p. 214 (1926).

obtaining the results are of equal accuracy in the two cases. This comparison is given in the following table :—

TABLE XII.

Gas.	$\sigma 10^8$ (1).	$\mu 10^{43}$ (1).	$\sigma 10^8$ (2).	$\mu 10^{43}$ (2).
Argon	3·13	·704	2·98	1·287
Nitrogen	3·38	·774	3·28	1·275

(1) From equation of state. (2) From viscosity.

A comparison of these results with those given in Table X. shows that closer values of σ and μ are obtained when the accurate formula of this paper is used instead of the approximate Sutherland formula.

The differences in the values of σ and μ given by the two methods point to the conclusion either that the molecular model chosen, viz. a rigid sphere plus an attractive field, is not a suitable one, or that the fields of force determined by the two methods are not strictly comparable *. No decision can be reached on this question until a more general theoretical formula for the variation of viscosity with temperature is obtained.

In this connexion it is interesting to note that in the case of helium it was found to be impossible to get any fit of the theoretical and experimental curves, which shows that a model of the Sutherland type is not applicable to helium. Presumably the same result is true for hydrogen also ; so that the molecular fields of these two gases can best be represented by repulsive forces varying inversely as a power of the distance, together with attractive fields which can be calculated from the equation of state of the gas, and which turn out to be weak compared with those of other gases. For this reason the variation of the viscosity with temperature depends solely on the repulsive force above mentioned, and this is of quite a different type to the concentrated repulsive effect given by the elastic sphere in the model of a molecule of the Sutherland type.

The University of Bristol,
January 1927.

* *Cf.* Lennard-Jones, *loc. cit.* p. 464.

XCV. *The Line Absorption Spectra of the Alkaline Earth Elements.* *By* O. H. Walters, *B.Sc.*, *and* S. Barratt, *B.A.*, *University College, London* *.

VERY few of the many recent investigations of metallic absorption spectra have included observations on the alkaline earth metals. McLennan and Young (Proc. Roy. Soc. 1919, A, xcv. p. 273) proved, from the ease of reversal of the 1S–mP series of calcium, strontium, and barium in an arc rich in the vapours of these metals, that the "normal state" of the atom is a 1S state. They did not observe in these experiments the reversal of any other lines of the metals. McLennan (Proc. Roy. Soc. 1916, A, xcii. p. 574) observed the absorption of the 1S–2P and 1S–3P lines of magnesium by a column of vapour; and it has since been found (Barratt, Proc. Roy. Soc. 1924, A, cv. p. 221) that λ 4571, the 1S–2p_2 line, is also absorbed, though not so readily. In the course of experiments on the band spectra associated with compounds of the alkaline earths, we have made numerous observations of the line absorption spectra of the vapours of these elements themselves. We have been able to amplify the foregoing data in certain directions, and in particular we have observed the absorption of series for which the Selection Rule governing changes of azimuthal quantum number does not hold.

The vapours were maintained in an iron tube of which the ends were water-cooled and closed by quartz windows, while the centre was heated by a nichrome-wound resistance furnace. The length of the heated portion of the tube was about 1 foot. The temperatures attained were not measured, but were estimated at about 1100° C. In most of the experiments the tube was filled with argon, to prevent rapid distillation of the metal to the cooled ends of the tube, but a sufficient number were carried out with the tube evacuated for it to be certain that the argon had no influence on the appearance of the spectra. The absorption was observed against the continuous spectrum from the crater of a carbon arc. Two Hilger spectrographs were used—a constant deviation instrument for the visible, and an "E 2" quartz model for the ultra-violet region. The wave-length range of the observations was 7000 A–2200 A. Magnesium and calcium were introduced into the tube in the form of metal. Strontium and barium,

* Communicated by the Authors.

however, are not commercial products, and some other procedure had to be adopted for these elements. Finally, their vapours were prepared *in situ* in the tube, by the reaction between calcium metal and strontium and barium halides. A very satisfactory column of strontium or barium vapour was always obtained in this way. The presence of calcium offered no difficulty, as the lines of this element could easily be recognized. It was found that lithium could replace the calcium, but its own band spectrum obscures a considerable wave-length range, and it was not employed for this reason.

Observations.

Calcium.—The first six members of the 1S–mP series—*i.e.* all those within the ultra-violet limit of the photographs—were found in absorption. The intensities assigned visually to the lines were as follows :—

4226·7 (20), 2721·6 (2), 2398·6 (5), 2275·5 (2),
2200·8 (1), 2150·8 (1).

It will be noticed that the second member is abnormally weak, in agreement with McLennan's observations on the arc absorption and with earlier observations of the same spectrum in emission. This line did not broaden so easily as the others. The line 1S–2p_2, λ 6572·8 was absorbed, but faintly in comparison with 1S–2P. The next member, 1S–3p_2, λ 2731·8 could never be detected on the plates, even when the density of the vapour was at its maximum, and λ 4226·7 was more than 50 A. broad. From previous observations on the alkali metal spectra, it seemed probable that the series 1S–mD would be found in the absorption spectra of the alkaline earths, and a careful search was made for the first member of the calcium series, λ 4575·4. It proved to be present on photographs taken through dense vapour, but it was unexpectedly faint. Its intensity was so low that care was necessary in obtaining a photograph suitable for measurement. It was observed visually on several occasions. The first member of the 1S–mF series, λ 2361·6, could not be detected.

Strontium.—Nine members of the 1S–mP series were recognized and were assigned the following intensities :—

4607·3 (20), 2931·9 (2), 2569·5 (5), 2428·1 (6), 2354·3 (6),
2307·4 (3), 2275·5 (*), 2253·3 (2), 2237·4 (1).

The intensity decrement is quite abnormal, as is that of corresponding calcium series.

1S–2p_2, λ 6892·6 was also found ; the second member,

* Coincident with calcium line.

λ 2855·3, is almost coincident with the magnesium resonance line and with a sodium line. Its presence is therefore uncertain.

The first line of the 1S–*m*D series, λ 4961·5, was also present. It was extremely weak and required dense vapour for its appearance.

No members of the 1S–*m*F series could be found.

Barium.—The first six lines of the 1S–*m*P series were found, as follows :—

5535·5 (20), 3071·6 (6), 2702·6 (2), 2596·7 (2), 2543·2 (1), 2500·2 (0).

The first members of the 1S–mp_2 and 1S–*m*D series were out of our wave-length range, and the second members were definitely not registered. Unlike the other elements, however, barium proved to absorb also the 1S–*m*F lines. Of these the first three were observed, always as sharp lines :—

3501·1 (3), 2785·3 (2), 2646·5 (1).

Magnesium.—The lines 1S–2P, λ 2852 and 1S–$2p_2$, λ 4571 were the only magnesium lines registered on the plates. The 1S–*m*D lines are all outside the wave-length range, and the F terms appear to be unknown.

Conclusions.

The absorption spectra of the vapours of the alkaline earth elements show the possibility of transitions of the series electron from its normal 1S orbit to orbits of the P, p_2, D, and F types. The transition to a D orbit has been observed in calcium and strontium vapours, and to an F orbit in barium vapour. The Selection Rule of unit change in the azimuthal quantum number evidently does not hold, and changes of 2 and 3 occur in the absence of any applied field. The series 1S–*m*P is the most readily absorbed, and many members of such series can easily be photographed. The widths of these lines are very sensitive to the partial pressure of the metal vapour ; this tendency to broaden would be expected by analogy with the behaviour of the corresponding series of the alkali metals. The 1S–mp_2 lines are always much fainter, and in our experiments we have never been able to observe more than the first member. The 1S–*m*D lines are even more weakly absorbed, and are in fact difficult to observe. The first three members of the 1S–*m*F series of barium are quite strongly in evidence, though the corresponding lines of the other elements are absent.

XCVI. *The Mathematical Theory of the Michell Ball Viscometer: with observations relating to its design, construction, and operation.* By Robert O. Boswall, *M.Sc. (Tech., Manch.), B.Sc. (Lond.), College of Technology, Manchester* *.

THE Michell cup-and-ball viscometer is now fairly well known as a simple type of instrument by means of which it is possible to determine the absolute viscosity of fluids—particularly lubricating oils—with a reasonable degree of accuracy, the usual experimental difficulties inherent to viscosity determinations being almost entirely avoided.

Its operation depends upon the fact that if two surfaces, initially separated by a very thin film of fluid, are pulled apart under the action of a constant force, then the time taken for separation to occur will be directly proportional to the absolute viscosity of the fluid. This assumes, of course, that the surfaces are immersed in the fluid so that the latter can flow into the space between the surfaces as they separate in order to maintain complete continuity of the film and also eliminate such interference effects as might result from the action of surface tension round the surface edges.

An explanation of the mathematical principles involved was apparently first given by Osborne Reynolds in his Royal Society paper on "The Theory of Lubrication" †, in which the special case of two plane elliptical surfaces is considered, and the relation between time of separation and film thickness shown to be expressible to a very close approximation by

$$t = \frac{3\pi}{2g} \cdot \frac{\lambda \cdot a^3 \cdot b^3}{\mathrm{F}(a^2+b^2)} \cdot \left\{ \frac{1}{\mathrm{H}_0^2} - \frac{1}{\mathrm{H}_t^2} \right\} \text{ seconds,} \quad . \quad (1)$$

where

λ = viscosity of the fluid in C.G.S. units,
F = force applied normal to the surfaces in grams,
a = semi-major axis of the ellipse in cm.,
b = semi-minor axis of the ellipse in cm.,
H_0 = initial film thickness in cm.,
H_t = final film thickness in cm.

* Communicated by the Author.
† Phil. Trans. 1886.

For circular plane surfaces, each having a radius of R cm., the expression becomes

$$t = \frac{3\pi}{4g} \cdot \frac{\lambda R^4}{F} \cdot \left\{ \frac{1}{H_0^2} - \frac{1}{H_t^2} \right\}. \quad . \quad . \quad . \quad (2)$$

It should be obvious from these equations that the time taken for separation increases very slowly as soon as the final film thickness exceeds about twenty times the initial thickness. In fact, all viscous restraint may be assumed to have ceased when the distance between the surfaces exceeds the limit stated. For instance, supposing that each surface had a radius of 1·0 cm. and the fluid had unit viscosity, then with a force of 60 grams and an initial film thickness of 0·001 cm. the time taken for separation would theoretically be 39·6 seconds when the final film thickness was 0·01 cm., 39·9 seconds when the thickness had increased to 0·02 cm., and only 40 seconds when the final distance between the surfaces was infinitely great.

For all practical purposes, therefore, the final film thickness need not be taken into account, and the time for complete separation may be written simply

$$T = \frac{3\pi}{4g} \cdot \frac{\lambda R^4}{F} \cdot \frac{1}{H_0^2} = k \cdot \lambda, \quad . \quad . \quad . \quad . \quad (3)$$

where k may be termed the surface constant.

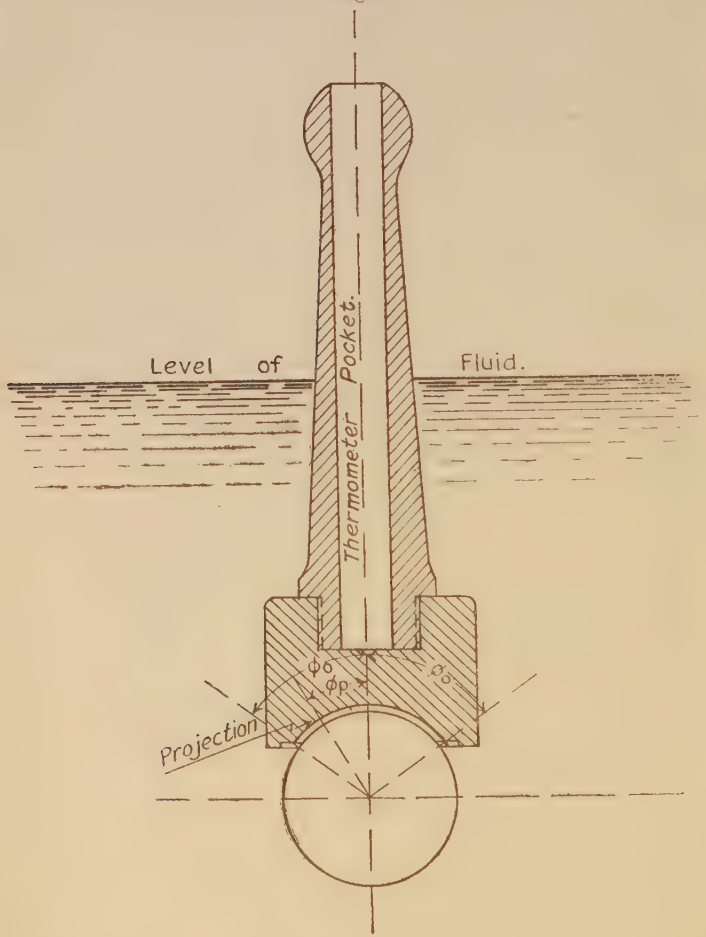
A very simple form of viscometer working on this principle might therefore be imagined to consist of two metal disks with corresponding plane surfaces, one of which would be provided with three or four minute projections for the purpose of regulating the initial film thickness. The plane of separation would, of course, be horizontal, and the constant force tending to separate the surfaces obtained by utilizing the weight of the lower disk.

In actual practice, however, the application of plane surfaces in this manner is open to the objection that any slight deviation of the plane of separation from the horizontal would immediately allow lateral or sliding motion to take place, and thus upset the whole theory upon which the successful operation of the instrument depends.

The practical form adopted, therefore, takes the shape of a hardened steel cup with a corresponding steel ball. The initial film thickness is suitably regulated by means of three minute projections or studs symmetrically spaced on the surface of the cup, and the weight of the ball is utilized for the constant force.

The arrangement of a typical instrument is shown in fig. 1, the cup being mounted on a handle provided with a thermometer pocket for the purpose of measuring temperature.

Fig. 1.



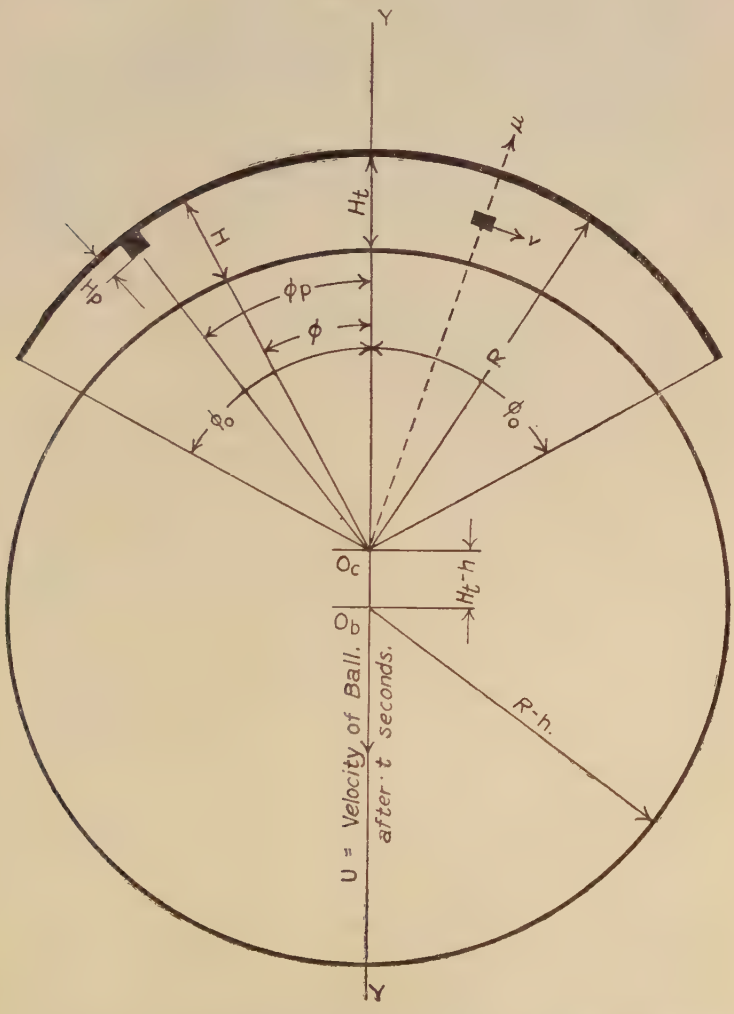
Although the actual working of the instrument is not materially altered by this modification, the adoption of spherical surfaces introduces certain features which have an important bearing not only upon the general design and proportions of the instrument, but also upon the limits of accuracy obtainable by its use.

This fact appears to have escaped previous notice, and

some additional explanation relating particularly to the application of curved surfaces seems desirable in view of the practical utility of the instrument.

Unfortunately, existing theory cannot be utilized for this purpose, and it will be necessary to refer back to first principles.

Fig. 2.



In fig. 2 is shown a cross-section through the spherical surfaces of a cup and ball which are supposed to be separated by a very thin film of some viscous fluid, the section being

taken in such a way that the centres of curvature of the surfaces, O_c and O_b, lie in its plane and also on the vertical axis of symmetry, YY.

The cup will be assumed to be stationary, and the ball, acting under the influence of its own weight, to move vertically downwards. Fluid will therefore be drawn from the bath in which the surfaces are supposed to be immersed, in order to fill up the gradually increasing space between them and thus maintain the continuity of the film.

This transverse or lateral inward flow of fluid between the surfaces sets up the condition of stress across the film which tends to oppose and thus control the motion of the ball.

Let R represent the radius of the cup, $(R-h)$ the radius of the ball, H_0 the initial film thickness at the centre of the cup measured along the axis YY, and H_t the corresponding thickness after an interval of t seconds from the commencement of separation.

Then, since the film thickness will always be very small compared with the radius of curvature of the surfaces, its value at any point subtending an angle θ with the vertical axis will be very approximately

$$H = (H_t - h)\cos\theta + h = \frac{h}{A_t}\{\cos\theta + A_t\}, \quad . \quad (4)$$

where A_t has been substituted for the term $\dfrac{h}{(H_t - h)}$.

In order to obtain the connexion between the various quantities involved, the usual equations for the viscous flow of fluids will be employed.

Using spherical polar notation with origin at the centre of the cup, and making the customary simplifying assumptions that

(a) the fluid adjacent to any surface has the velocity of that surface ;

(b) the velocity u of any fluid element in the radial direction is small compared with its velocity in the tangential direction :

(c) variations of the tangential velocity in the tangential direction are negligible compared with corresponding variations in the radial direction ;

(d) there is no rotational motion of the fluid between the surfaces, *i. e.* the velocity w is zero ;

(e) the pressure variation in the radial direction is zero, since the film is very thin ;

it follows that, if P represents the intensity of stress and λ the viscosity for any fluid element, then

$$\frac{1}{r}\cdot\frac{dP}{d\theta}=\frac{\lambda}{r^2}\cdot\frac{d}{dr}\left(r^2\cdot\frac{dv}{dr}\right), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{dP}{dr}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Since the intensity of stress is not a function of r, the value of the tangential velocity v can be obtained by the direct integration of equation (5), the necessary constants being ascertained from the boundary conditions; that is to say, if U represents the velocity with which the ball moves vertically downwards at any instant, then at the surface of the cup where $r=R$, $v=0$, and at the surface of the ball where $r=(R-H)$, $v=U\,.\sin\theta$.

This gives

$$v=\frac{1}{2\lambda}\cdot\frac{dP}{d\theta}\cdot\frac{(r-R)(r-R+H)}{r}-\frac{U\,.\sin\theta\,.(R-H)(r-R)}{H\,.r}. \quad (7)$$

If this value is now substituted in the continuity equation

$$\frac{1}{r^2}\cdot\frac{d}{dr}(u\,.r^2)+\frac{1}{r\,.\sin\theta}\cdot\frac{d}{d\theta}(v\,.\sin\theta)=0, \quad . \quad (8)$$

and the resulting equation is integrated with respect to r and θ, it will be found, on omitting certain negligible terms involving the film thickness H, that

$$\frac{dP}{d\theta}=\frac{6\lambda R^2U\sin\theta}{H^3}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The intensity of stress in dynes per sq. cm. at any point in the film is consequently

$$p=p_0-\frac{3\lambda R^2UA_t^3}{h^3}\left\{\frac{1}{(\cos\theta_0+A_t)^2}-\frac{1}{(\cos\theta+A_t)^2}\right\}, \quad (10)$$

where p_0 represents the intensity of pressure at the outer edge of the film due to its depth of immersion in the bath, and θ_0 represents the angle subtended between any radius to the edge of the cup and the vertical axis of symmetry YY.

The vertical component of the intensity of stress at any point is $p\,.\cos\theta$. On integrating this across the surface of the film, it will be found that the vertical resultant force

controlling the motion of the ball takes the form

$$P=\pi R^2\left\{p_0.\sin^2\theta_0-\frac{3\lambda R^2 U A_t^3 B}{h^3}\right\}, \quad . \quad . \quad (11)$$

where

$$B=\frac{\sin^2\theta_0}{(\cos\theta_0+A_t)^2}+2\log_e.\frac{(\cos\theta_0+A_t)}{(1+A_t)}+\frac{2A_t(1-\cos\theta_0)}{(1+A_t)(\cos\theta_0+A_t)} \quad . \quad . \quad . \quad (12)$$

The external force exerted by the ball will now be considered. In doing this, allowance must be made for the fact that it is immersed in the fluid, and is also partly shielded on its upper surface by the cup.

Thus, if ρ and σ represent the respective densities of the ball and fluid in grams per cu. cm., the actual effective force will be

$$F=\pi R^2\left\{\frac{RgC}{3}-p_0.\sin^2\theta_0\right\}, \quad . \quad . \quad . \quad (13)$$

where

$$C=4\rho-(2+3\cos\theta_0-\cos^3\theta_0)\sigma. \quad . \quad . \quad (14)$$

Strictly speaking, part of this effective force is utilized in accelerating the ball, and also in overcoming the resistance offered to its motion by the fluid in which it is immersed. The inclusion, however, of these acceleration and resistance terms renders subsequent integration difficult, and since both are small in comparison with the other forces acting, their effect will be considered negligible, and equilibrium will be assumed to be established when

$$P+F=0; \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

that is to say, when

$$g.C-\frac{9\lambda RUA_t^3B}{h^3}=0, \quad . \quad . \quad . \quad . \quad (16)$$

the vanishing of the term involving p_0 indicating that it is quite immaterial to what depth the cup and ball are immersed provided that the edge of the cup is always completely covered in order to ensure complete continuity of the film during the process of separation.

The displacement of the centre of the ball during the time interval of t seconds is (H_t-H_0), and its velocity can therefore be expressed in the form

$$U=\frac{dH_t}{dt}.$$

If this value for U is now substituted in (16) and the

resulting equation integrated, it will be found that the required relationship between time and film thickness takes the form

$$T = -\frac{9\lambda R}{g \cdot C} \cdot \frac{1}{h^2} \left\{ (1 + A_t^2) \cdot \log_e \frac{(\cos\theta_0 + A_t)}{(1 + A_t)} + \frac{A_t(A_t - 1)(1 - \cos\theta_0)}{(\cos\theta_0 + A_t)} \right\}, \quad (17)$$

the limits for the term A_t being $\left(\frac{h}{H_0 - h}\right)$ and $\left(\frac{h}{H_T - h}\right)$.

If the final film thickness H_T is assumed to be relatively large compared with the initial thickness H_0, the time taken for complete separation approximates very closely to

$$T = \frac{9 \cdot \lambda \cdot R}{g \cdot C} \cdot \frac{1}{h^2} \quad (1 + A_0^2) \cdot \log_e \cdot \frac{(\cos\theta_0 + A_0)}{(1 + A_0)} + \frac{A_0(A_0 - 1)(1 - \cos\theta_0)}{(\cos\theta_0 + A_0)} - \log_e \cos\theta_0 \Big\}, \quad (18)$$

and is the form in which the equation will be used. It fails however, to apply in the two special cases for which either $(H_0 - h)$ or h happens to be zero. These must therefore be considered separately, and it will be found that in the former case equation (18) takes the limiting value

$$T = -\frac{9 \cdot \lambda \cdot R}{2 \cdot g \cdot C} \cdot \frac{1}{h^2} \{2 \cdot \log_e \cdot \cos\theta_0 + \sin^2\theta_0\}, \quad . \quad (19)$$

whilst for the latter case, in which both cup and ball have the same radius,

$$T = \frac{9 \cdot \lambda \cdot R}{2 \cdot g \cdot C} \cdot \frac{1}{H_0^2} \cdot \{2 \log_e \cos\theta_0 + \tan^2\theta_0\}. \quad . \quad (20)$$

The last three expressions can all be written in the general form

$$T = k \cdot \lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

in which the coefficient k depends upon the dimensions of the instrument, and will be termed the instrument constant.

Since it is impossible to directly measure with any degree of accuracy such minutely small dimensions as the initial thickness of the film and the difference in radius between the surfaces, the value of the constant has to be obtained by calibrating the instrument with an oil or other fluid of known viscosity. This is usually done for one temperature only, and the result is assumed to be correct for any other temperature.

In certain instances, however, it has been found that although viscosity observations made at any one temperature with an instrument calibrated in this manner gave reasonably consistent results, this was not always the case when a series of observations was taken over a range of temperature. The irregularities noticed could not be directly attributed to experimental errors, and gave the impression that the changes in temperature must in some way be responsible for alterations in the value of the constant.

For this explanation to hold good, it would have to be proved that the instrument constant was very sensitive to extremely small changes in the dimensions of the instrument.

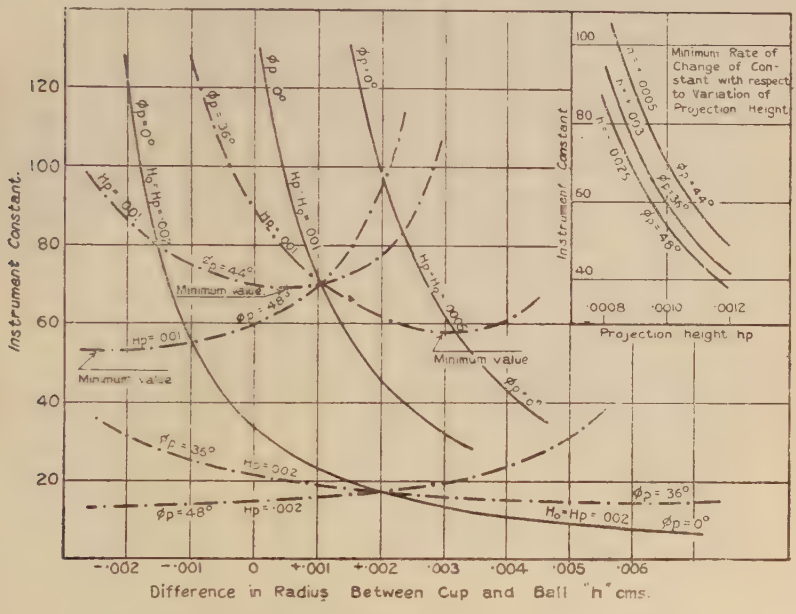
Values of the constant corresponding to various initial film thicknesses and differences of radius have therefore been calculated for a standard type of instrument in which the ball has a radius of 1·27 cm. (1·0 inch diameter) and $\phi_0 = 52°$, the projected area of the film surface in this case being a circle of 1·0 cm. radius. In addition, the density of the ball and fluid are assumed to be 8·0 and 0·9 grams per c.c. respectively.

These values are represented by the continuous lines in fig. 3. The shape of these curves clearly indicates that large changes may take place in the value of the constant if either the initial film thickness at the centre of the cup or the difference in radius is altered, the effect being particularly noticeable when the film is initially very thin and the instrument constant fairly large. Taking, for example, the case in which the initial film thickness is 0·001 cm., it will be found that when both cup and ball have the same radius, *i. e.* when "h" is zero, the constant changes at the rate of roughly 8 per cent. per 0·0001 cm. variation in the difference of radius. A change of this magnitude would account for the discrepancies noticed, and might possibly be produced by thermal expansion or distortion of the surfaces.

Assuming, for instance, that the linear coefficient of expansion for steel is 0·000007 per degree Fahr., a change of 0·0001 cm. on an initial radius of 1·27 cm. might occur for a change in temperature of about 12° F. This change should, of course, affect both cup and ball to the same extent, in which case there would be no actual change in the radial difference, and therefore no change in the value of the constant. The shape of the cup and its mounting, however, renders it liable to irregular expansion or distortion, and there is always the additional possibility of this being further influenced by any dissimilarity in material or the presence of a temperature gradient across the metal.

As the initial film thickness increases and the value of the instrument constant decreases, errors due to change of radius tend to diminish. For instance, when the initial film thickness at the cup centre is 0·002 cm., the variation in the value of the constant per 0·0001 cm. change in the difference of radius is only about 4 per cent., or half as great as in the previous case.

Fig. 3.


Instrument Constant.
120
100
80
60
40
20
Minimum value
Minimum value
Minimum value
Minimum value
Hp=·001
Hp=·002
Hp=·002
Hp=·002
Hp=·001
Hp=·001
Hp=·001

between each of the projections and the vertical axis YY, then the film thickness at the centre of the cup can be expressed in the form

$$H_0 = \frac{H_p - h(1-\cos\theta_p)}{\cos\theta_p} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Since the height of the projections is fixed for any one instrument, the value of the constant is obviously dependent upon the position-angle θ_p, and it is possible to show that small changes in the difference of radius between cup and ball can, within certain limits, be almost entirely eliminated if the position of the projections is suitably chosen.

This can be explained most readily by a graphical method. Values of H_0 corresponding to certain values of the dimensions H_p, θ_p, and the radial difference h, have therefore been calculated from (22), and the results interpolated with the curves already drawn in fig. 3.

In this way a series of transverse lines is obtained, each line corresponding to a fixed projection-height and position-angle. The U-shape of these new curves—which are shown chain-dotted—indicates that the instrument constant in each case has a minimum value. For an instrument to give consistently reliable results and be, as far as possible, independent of variations in the radial dimensions, it is clearly essential that the value for its constant should coincide with one of these minimum values in order that the rate of change of the constant with respect to change of radius may be as small as possible. That is to say, the instrument should be so proportioned that the height of each of the projections and the initial difference of radius are associated as far as is practicable with the correct corresponding position-angle.

Thus, when H_p is 0·001 cm. and θ_p is 36°, a reasonable degree of accuracy will only be attainable when the radial difference is approximately 0·003 cm. (see fig. 3), and the minimum value of the constant is about 59. Similarly, for the same projection-height but with position-angles of 44° and 48°, the necessary conditions are only satisfied if the radius of the cup in the first case is 0·0005 cm. greater, and in the second case 0·0025 cm. smaller, than the ball, the corresponding minimum values for the constant being approximately 70 and 53. In these two instances the flattening of the curves in the neighbourhood of the minimum value indicates a marked improvement in the accuracy obtainable. This effect becomes even more pronounced as the projection-height is increased and the instrument constant is lowered, the curves drawn for a projection-height of 0·002 cm. showing

that the probable error due to change of constant is practically negligible over quite a wide range of radial difference.

For the special case in which both cup and ball have the same initial radius, it can be shown that the constant will have a minimum value when the position-angle for each projection is given by

$$\cos\theta_p = \frac{3\cos^2\theta_0(\tan^2\theta_0 + 2\log_e.\cos\theta_0)}{2(1-3\cos^2\theta_0+2\cos^3\theta_0)}, \quad . \quad (23)$$

the height of the projections having no effect. Thus, when the angle θ_0 to the cup-edge is 52°, as in the numerical case cited, the correct position-angle for each projection will be almost exactly 45° for all projection-heights.

In addition to the effect of variations in the difference of radius, it must also be noted that very small variations in the height of the projections themselves may be responsible for relatively large changes in the value of the constant. This is shown graphically in fig. 3*a*, where some supplementary curves have been drawn to indicate the relation between the constant and the height of the projections for three different position-angles, the instrument in each case being assumed to be correctly proportioned, *i. e.* to have a minimum value for its constant, when the initial or normal projection height is 0·001 cm.

The slope of these curves shows that the constant is very sensitive to changes of this character. The sensitivity, however, gets less as the projection-heights increase and the constant decreases.

Temperature changes in this case would probably be negligible. The presence, however, of minute particles of grit, fibrous material, or other matter between the projections and the surface of the ball would be liable to seriously influence the accuracy of the instrument, the effect being more particularly noticeable in the case of high-constant instruments when the fluid film is very thin at the commencement of separation.

It would appear, therefore, that although the Michell viscometer may be regarded from a purely theoretical standpoint as a precision instrument, it can only be actually applied in practice to measure viscosity over a range of temperature with any degree of accuracy if certain conditions of a practical character are more or less closely fulfilled. These may be briefly summarized as follows:—

(1) In order that there is the least possible change of constant with change of radius, the projections used for

regulating the initial film thickness at the centre of the cup must be correctly spaced to suit the initial difference in radius and the height of projection. This is a difficult practical condition which cannot easily be satisfied, and the simplest way out of the difficulty would probably be to obtain surfaces having equal radius and to space the projections in accordance with the value given in (23) for the position-angle.

(2) Both cup and ball should be made of similar material to avoid unequal expansion, and particular attention should be paid to getting a suitable shape for the cup-mounting in order that irregular expansion or distortion may be reduced to a minimum. In connexion with this point, it may be noted that a rise in temperature of 3° Fahr. will produce a linear expansion of about 0·00002 cm. per cm.

(3) The instrument should be calibrated with an oil or other fluid of known viscosity over a range of temperature, any variation in the value of the constant being carefully recorded.

(4) Other things being equal, a low-constant instrument should give better accuracy than one having a high constant. The term high constant is applied to an instrument having a constant exceeding about 40.

(5) The use of a high-constant instrument with thick or very viscous fluids should be avoided as far as possible. In any case, the fluid to be tested should be strained or allowed to stand for sufficient time to allow particles of foreign matter to settle down.

(6) When taking a series of observations over a range of temperature, special care must be taken that the rate of cooling is very slow and that the temperature is uniform throughout the fluid in the bath.

(7) The depth to which the instrument is immersed in the bath does not affect the accuracy of the instrument, provided that the edge of the cup is completely covered.

It is hoped that the foregoing notes, although of a necessarily theoretical nature, may prove to be of some use to those responsible for the design and construction of these very useful little instruments as well as to those who may have occasion to use them.

In conclusion, the writer would like to take this opportunity of expressing his indebtedness to Prof. G. Stoney, D.Sc., F.R.S., for the interest he has taken in the preparation of this paper and for much valuable criticism and advice.

XCVII. *The Calculation of Determinants and their Minors.* *By* T. Smith, *M.A., F.Inst.P.* (*From the National Physical Laboratory.*)*

Abstract.

A routine method of building up the adjugate determinant is described, the order at each successive stage being increased by unity.

Numerical determinants of high orders are usually evaluated by processes which enable the order to be reduced until a simple determinant, the value of which may be written down by inspection, is reached. When it is desired to find the values, not merely of the complete determinant, but also of all its first minors, this procedure appears to involve more labour than is necessary. The converse method of building up the adjugate determinant in stages has been found advantageous; one of its merits is that the calculations may be safely entrusted to untrained workers.

Suppose that the adjugate of the determinant Δ_{n-1} consisting of the first $n-1$ rows and columns of the given determinant has been found. Let it be

$$\begin{vmatrix} A_{1,1} & A_{1,2} & A_{1,3} & \dots & A_{1,n-1} \\ A_{2,1} & A_{2,2} & A_{2,3} & \dots & A_{2,n-1} \\ \dots & \dots & \dots & \dots & \dots \\ A_{n-1,1} & A_{n-1,2} & A_{n-1,3} & \dots & A_{n-1,n-1} \end{vmatrix}$$

The adjugate

$$\begin{vmatrix} B_{1,1} & B_{1,2} & B_{1,3} & \dots & B_{1,n-1} & B_{1,n} \\ B_{2,1} & B_{2,2} & B_{2,3} & \dots & B_{2,n-1} & B_{2,n} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ B_{n-1,1} & B_{n-1,2} & B_{n-1,3} & \dots & B_{n-1,n-1} & B_{n-1,n} \\ B_{n,1} & B_{n,2} & B_{n,3} & \dots & B_{n,n-1} & B_{n,n} \end{vmatrix}$$

* Communicated by the Author.

of the determinant Δ_n formed by adding the nth row and column

$$\begin{matrix} & & & & a_{1,n} \\ & & & & a_{2,n} \\ & & & & \cdots \\ & & & & a_{n-1,n} \\ a_{n,1} & a_{n,2} & a_{n,3} & \cdots\cdots & a_{n,n} \end{matrix}$$

has now to be found. The first step is to evaluate the B's which have n as one of their suffixes. These are found from the equations :

$$\left.\begin{aligned} B_{p,n} &= -\sum_{1}^{n-1} a_{n,q} A_{p,q} \\ B_{n,p} &= -\sum_{1}^{n-1} a_{q,n} A_{q,p} \end{aligned}\right\} \quad \cdots\cdots \quad (1)$$

$$B_{n,n} = \Delta_{n-1}.$$

The value of Δ_n is derived at once from one of the equations

$$\Delta_n = \sum_{1}^{n} a_{p,n} B_{p,n} = \sum_{1}^{n} a_{n,p} B_{n,p},$$

and the remaining B's from

$$\Delta_{n-1} B_{p,q} = \Delta_n A_{p,q} + B_{p,n} B_{n,q}. \quad \cdots\cdots \quad (2)$$

It will be observed that, when the elements of the original determinant are integral, any errors in calculation (as distinct from errors due to taking incorrect values for these elements) are likely to be revealed at once by fractional values being found for some of the B's by equation (2).

The proof of the method merely involves the demonstration of formulæ (1) and (2). Evidently the terms of Δ_n involving $a_{p,n}$ are obtained by writing $a_{p,q} a_{n,n} - a_{p,n} a_{n,q}$ for $a_{p,q}$ in Δ_{n-1}, where q is given in turn the values $1, 2, \ldots\ldots n-1$. Thus

$$\begin{aligned} B_{p,n} &= \text{coefficient of } a_{p,n} \text{ in } \sum_{1}^{n-1} (a_{p,q} a_{n,n} - a_{p,n} a_{n,q}) A_{p,q} \\ &= -\sum_{1}^{n-1} a_{n,q} A_{p,q}, \end{aligned}$$

which is the first relation in (1); the second obviously

follows from symmetry. It will suffice to prove (2) for $p=q=1$. Then

$$\overset{n-1}{\Delta}_{n-1}B_{1,1}=$$

$$\begin{vmatrix} A_{1,1} & A_{1,2} & \dots & A_{1,n-1} & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ A_{n-1,1} & A_{n-1,2} & \dots & A_{n-1,n-1} & 0 \\ B_{n,1} & B_{n,2} & \dots & B_{n,n-1} & B_{n,n} \end{vmatrix} \begin{vmatrix} 1 & 0 & \dots & 0 \\ a_{2,1} & a_{2,2} & \dots & a_{2,n} \\ \cdot & \cdot & \cdot & \cdot \\ a_{n,1} & a_{n,2} & \dots & a_{n,n} \end{vmatrix}$$

$$= \begin{vmatrix} A_{1,1} & A_{2,1} & A_{3,1} & \dots & A_{n-1,1} & B_{n,1} \\ 0 & \Delta_{n-1} & 0 & \dots & 0 & 0 \\ 0 & 0 & \Delta_{n-1} & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \dots & \Delta_{n-1} & 0 \\ -B_{1,n} & -B_{2,n} & -B_{3,n} & \dots & -B_{n-1,n} & \Delta_n \end{vmatrix}$$

by the multiplication theorem and (1); that is

$$\Delta_{n-1}B_{1,1}=\Delta_n A_{1,1}+B_{1,n}B_{n,1}.$$

Alternatively (1) and (2) may be verified by deriving the relations

$$\sum_1^n B_{p,q}a_{p,r}=0 (q\neq r) \quad \text{and} \quad \sum_1^n B_{p,r}a_{p,r}=\Delta_n$$

from the corresponding A equations.

In dealing with determinants of very high orders it will be advantageous to add borders of higher order than the first, but the method then loses the simplicity which renders it suitable for use by those who have no theoretical knowledge of the subject.

XCVIII. *The Ratio of the Numbers of Resonating Electrons for the Potassium Doublets.* *By* V. K. Prokofiev *.

Summary.

From measurements of the dispersion of potassium vapour in the regions of the first and second doublets of the principal series it is shown that the ratio of the numbers of resonating electrons corresponding to the two doublets is 110 to 1, and does not depend upon the density of the vapour. The corresponding measurements of this ratio for the individual lines of each doublet are 1·995 to 1 for the red doublet, and 2·046 to 1 for the violet doublet.

1. *Introduction.*

THE classical theory of anomalous dispersion leads to Sellmeier's formula which holds for regions remote from the absorption lines :

$$n^2-1=\Sigma\frac{a_i\lambda^3}{\lambda^3-\lambda_i^2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where λ_i denotes the wave-length corresponding to the free vibrations of the electron within the atom, the constant a_i being given by

$$a_i=\frac{\rho_i\lambda_i^2}{8\pi^2c^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$\rho_i=\frac{4\pi N_i e^2}{m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

c being the velocity of light, e and m the charge and mass of the electron respectively, and N_i the number of absorbing electrons per c.c.

It is possible to calculate the number of resonating electrons N per c.c. by measuring the refractive index n for different values of λ, and to compare these numbers thus obtained with the number of atoms as determined from vapour-density measurements.

Ladenburg and Minkowski † by means of measurements of the magnetic rotation of the plane of polarization in the immediate neighbourhood of the D lines determined the numbers N_1 and N_2 corresponding to the two D lines, and the value of N_1+N_2 was equal to the number of sodium atoms per c.c. This result, which is only approximately

* Communicated by the Author.

† *Zeits. f. Physik,* vi. 2. p. 153 (1921).

true, can be explained, either by supposing that there are two sets of sodium atoms, each set corresponding to a line of the doublet, or by postulating that all the atoms are alike, but that the electron of each atom can vibrate in either of two ways corresponding to the D_1 and D_2 lines. If this second supposition is adopted the ratio $\frac{N_1}{N_2}$ must be regarded as an atomic constant, independent of vapour pressure and temperature. The value of this ratio has been determined at various pressures for sodium by Minkowski * and Rogestwenski †. Rogestwenski ‡ has also determined its value for potassium, rubidium, and cæsium. All these results give the ratio as 2 and show that it is independent of vapour density and temperature. It is natural, therefore, to suppose that this ratio denotes an atomic constant, and that absorption of light, corresponding to both lines of the first doublet of the principal series, is a process occurring within the atom of the alkali metal.

Unfortunately the value of $N_1 + N_2$ diminishes rapidly in passing from the first doublet to the others, so that previous measurements do not show whether the absorption for all the doublets of the principal series is due to one single atom or to several.

A more promising line of investigation is the measurement of the ratio $\frac{(N_1+N_2)_A}{(N_1+N_2)_B} = \sigma$ at different pressures and temperatures, where the suffixes A and B refer to the first and second doublets. This has been done by various experimenters, but the results obtained do not agree. Bevan §, using crossed prisms, found that the value of σ varied with the vapour density; on the other hand, Rogestwenski ‖, working with a spectrograph of high resolving power, proved that for potassium the value of σ was constant over an eight-fold vapour-density variation. Miss Baxter ¶ compared the first and second doublets of potassium, and found that the value of σ decreased as the vapour density increased. Her measurements were made with a Jamin interferometer and a spectrograph of small resolving power, the absorption lines appearing on the plates at the extremities of the visible spectrum. The dispersion was observed in the

* *Ann. d. Phys.* lxvi. p. 206 (1921).
† *Ann. d. Phys.* xxxix. p. 307 (1912).
‡ Trans. Opt. Inst. ii. N. 13 (Leningrad).
§ Proc. Roy. Soc. A, lxxxiv. p. 209 (1911), and lxxxv. p. 58 (1911).
‖ Trans. Opt. Inst. ii. N. 13 (Leningrad).
¶ Phil. Mag. xlii. p. 289 (1921).

visible part of the spectrum at a considerable distance from the absorption lines.

The results of these investigations are therefore contradictory, and it was decided to investigate the dependence of the ratio σ on the vapour density. The temperature effect was considered only in as much as it affected the vapour density, and it was thought sufficient to investigate one pair of doublets only in the vapour of one alkali metal. The result can then be applied to all series of all the alkali metals. Potassium was chosen for the experiments as the first two doublets of the principal series are easily observed, since they appear at the extremities of the visible spectrum, their wave-lengths being 7664·91, 7699·08 Å and 4044·32, 4047·37 Å.

2. *Method of Investigation.*

The method of investigation is that given by Rogestwenski*. The horizontal equidistant interference fringes from a Jamin interferometer are projected on the slit of a high resolving power spectrograph. If the ordinate y is measured from the point where the path difference is nil, the formula for the path difference becomes

$$\Delta = by,$$

where b is a constant.

For maximum intensity

$$by = k\lambda,$$

where k denotes the order of the fringe measured from the zero one. If we introduce in the path of one of the interfering rays a column of vapour of length d and refractive index n, then the path difference

$$(n-1)d = f(\lambda)d$$

and

$$df(\lambda) = k\lambda.$$

For the zero fringe $k = 0$ we can write

$$y = \frac{d}{b} f(\lambda),$$

i. e. the zero fringe determines the shape of the dispersion curve (see fig. 1 *a*, curves A).

If in the path of the second interfering ray we place a

* Trans. Opt. Ins. ii, N, 13 (Leningrad).

plane parallel glass plate of thickness d_1, such a plate produces a large path difference $d_1 r(\lambda)$. Without the presence of the vapour the fringes produced by $r(\lambda)d_1 = k\lambda$ would at every point have a great inclination (see fig. 1 *a*, fringes B) but in the opposite direction to that of the fringes A produced by the anomalous dispersion. The simultaneous action of

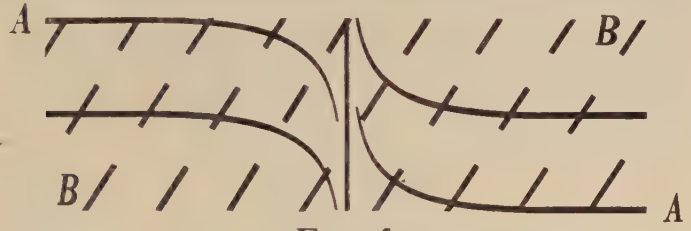


Fig. 1a.

the anomalous dispersion and the great path difference neutralizes the inclination of the interference curves at two points, and curves of another shape result, similar to those shown in fig. 1 *b*, having characteristic maxima and minima

Fig. 1b.

near the absorption line. These curves will be referred to as "hooks." They are represented by the equation

$$d_1 r(\lambda) - df(\lambda) = k\lambda. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The wave-lengths corresponding to the hooks can be obtained from the condition

$$\frac{\partial y}{\partial \lambda} = 0,$$

i. e.

$$\frac{\partial f(\lambda)}{\partial \lambda} = \frac{d_1 \dfrac{\partial r(\lambda)}{\partial \lambda} - k}{d}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $f(\lambda)$ is given by equation (1). In the proximity of a doublet it is sufficient to take only two members of the sum.

Near each line of the doublet two hooks appear, and if we measure their distance from the absorption lines in wavelengths, and also the distance between the absorption lines, we can obtain the constants a_1 and a_2 of equation (1).

Since the distance between the external hooks never exceeds 50 A, we may consider $\frac{\partial r(\lambda)}{\partial \lambda}$ constant, and the path difference $df(\lambda)$ produced by the vapour being very small in comparison with the path difference $d_1 r(\lambda)$, we can use in the neighbourhood of the axis where y is very small the value of k given by equation (4), viz.,

$$k = \frac{d_1 r(\lambda)}{\lambda}.$$

Moreover, the value $\frac{r(\lambda)}{\lambda}$ varies by less than 1 per cent. in the region under consideration, and for one doublet therefore we can take $\frac{r(\lambda)}{\lambda}$ and $\frac{\partial r(\lambda)}{\partial \lambda}$ for a certain mean wavelength λ_0. We then obtain

$$-\frac{\partial f(\lambda)}{\partial \lambda} = \left[\frac{r(\lambda_0)}{\lambda_0} - \left(\frac{\partial r(\lambda)}{\partial \lambda}\right)_0\right]\frac{d_1}{d} = \frac{K}{d},$$

where K is a constant for the given doublet and can be calculated or measured with sufficient accuracy.

Within the range of measurements λ varies very little and $n-1$ is small so that equation (1) can be simplified by taking

$$f(\lambda) = \frac{a_1\lambda_1}{2(\lambda-\lambda_1)} + \frac{a_2\lambda_2}{2(\lambda-\lambda_2)},$$

and we obtain

$$\frac{1}{2}\frac{a_1\lambda_1}{(\lambda-\lambda_1)^2} + \frac{1}{2}\frac{a_2\lambda_2}{(\lambda-\lambda_2)^2} = \frac{K}{d}.$$

This equation has in general 4 roots corresponding to 4 hooks. Denoting these roots by ${}_1\lambda$, ${}_2\lambda$, ${}_3\lambda$, and ${}_4\lambda$, and writing

$$\left.\begin{aligned} &\lambda_1 - {}_1\lambda = \delta_1, \quad {}_2\lambda - \lambda_1 = \delta_2, \quad \lambda_2 - {}_3\lambda = \delta_3, \quad {}_4\lambda - \lambda_2 = \delta_4, \\ &\lambda_2 - \lambda_1 = \epsilon, \quad \alpha_1 = \frac{a_1\lambda_1 d}{2K\epsilon^2}, \qquad \alpha_2 = \frac{a_2\lambda_2 d}{2K\epsilon^2}, \end{aligned}\right\} \quad (6)$$

where δ is the distance of the hook from the corresponding

absorption lines and ϵ the distance between the two absorption lines, then

$$\alpha_1 = \frac{\delta_1\delta_2}{\epsilon^2} \times \frac{1}{1+\Delta_1}; \quad \alpha_2 = \frac{\delta_3\delta_4}{\epsilon^2} \times \frac{1}{1+\Delta_2}, \quad . \quad . \quad (7)$$

where Δ_1 and Δ_2 are correction terms which account for the influence of the dispersion produced by the second line on the distance of the hooks from the other line. These correction terms are given by

$$\Delta_1 = \frac{\dfrac{\delta_3\delta_4}{\epsilon^2}}{1-\dfrac{\delta_1\delta_2+\delta_3\delta_4}{\epsilon^2}}, \qquad \Delta_2 = \frac{\dfrac{\delta_1\delta_2}{\epsilon_2}}{1-\dfrac{\delta_1\delta_2+\delta_3\delta_4}{\epsilon^2}}.$$

For large values of the vapour density the dispersion curve inside the red doublet is nearly vertical, and the thickness of the glass plate is not sufficient to produce a greater inclination to the opposite side; in such a case no hooks can be observed inside the pair of lines, and only two hooks are produced, δ_1 and δ_4, the two other roots of the equation, δ_2 and δ_3, being imaginary. From these results

$$\alpha_1 = \frac{\left(1+\dfrac{\delta_1}{\epsilon}\right)^2 - \dfrac{\delta_4^2}{\epsilon^2}}{\left(1+\dfrac{\epsilon}{\delta_1}\right)^2 - \dfrac{1}{\left(1+\dfrac{\epsilon}{\delta_4}\right)^2}}, \qquad \alpha_2 = \frac{\left(1+\dfrac{\delta_4}{\epsilon}\right)^2 - \dfrac{\delta_1^2}{\epsilon^2}}{\left(1+\dfrac{\epsilon}{\delta_4}\right)^2 - \dfrac{1}{\left(1+\dfrac{\epsilon}{\delta_1}\right)^2}}$$

and

$$\frac{\alpha_1}{\alpha_2} = \frac{\dfrac{\epsilon^2}{\delta_4^2} - \dfrac{1}{\left(1+\dfrac{\delta_1}{\epsilon}\right)^2}}{\dfrac{\epsilon^2}{\delta_1^2} - \dfrac{1}{\left(1+\dfrac{\delta_1}{\epsilon}\right)^2}}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The results obtained from these formulæ are not as accurate as those given by formula (7). As the ratio $\frac{\rho_1}{\rho_2}$ for the two lines of a doublet is constant then σ may be written

$$\sigma = \frac{(N_1+N_2)_A}{(N_1+N_2)_B} = \frac{(\rho_1+\rho_2)_A}{(\rho_1+\rho_2)_B} = \frac{(\alpha_1+\alpha_2)_A}{(\alpha_1+\alpha_2)_B} \cdot \frac{K_A}{K_B} \cdot \frac{\lambda_B^3}{\lambda_A^3} \cdot \frac{\epsilon_A^2}{\epsilon_B^2}. \quad (9)$$

The letter suffixes denote the different doublets in the principal series.

The ratio $\frac{\rho_1}{\rho_2}=\frac{N_1}{N_2}$ was measured at the same time for each doublet, its value being 2, within the limits of observation errors, and finally the value ρ_1 for the line λ_1 of the greater refractive in the red doublet is

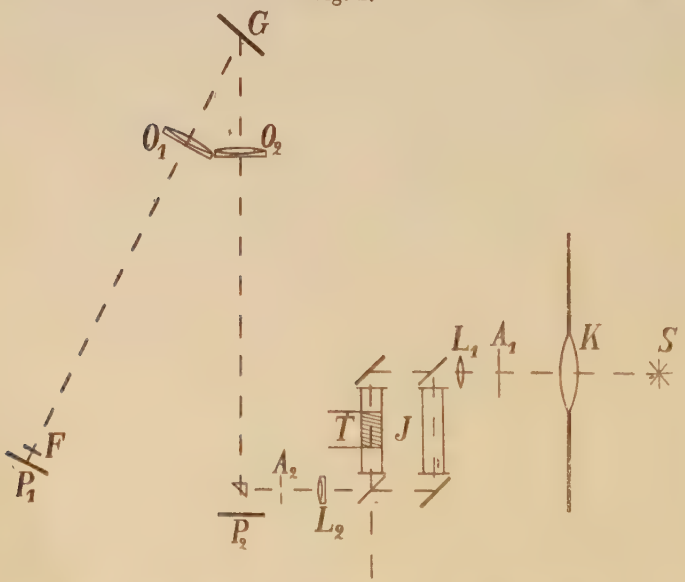
$$\rho_1=\frac{16\pi^2c^2}{d\lambda_1^3}\cdot K_1\cdot\epsilon_1^2\cdot\alpha_1,$$

which gives, approximately, the vapour density, the value of d not being known with any great degree of accuracy. In obtaining the ratios σ and $\frac{\rho_1}{\rho_2}$, d is eliminated by photographing the doublets simultaneously.

3. *Arrangement of Apparatus.*

The apparatus used, shown diagrammatically in fig. 2,

Fig. 2.



differs very little from that used by Rogestwenski. The source of light, S, was an electric arc with horizontal electrodes, and was placed in a room adjacent to the one in which the interferometer was situated. The light reached the point A_1 through a condenser K inserted in the communicating door, and a parallel pencil of light was admitted to the interferometer through the lens L_1.

The Jamin interferometer used was arranged so that there was a considerable distance between the two interfering beams, the usual glass plates being replaced by a system of a plane silvered mirror and a plane-parallel half-silvered glass plate. In both systems the distance between mirror and plate was equal. In order to avoid external vibrations, as far as possible, the interferometer was placed on a table having as base a stone plate weighing about 110 kilograms. This plate rested on four rubber supports.

An electrically heated quartz tube containing potassium was placed in one beam of light and an evacuated glass tube in the other, both tubes being sealed with perfectly plane-parallel glass plates.

The interferometer gave two systems of interference fringes reflected on, and transmitted through, the last half-silvered plate. The transmitted system, projected on a screen, was used to follow visually the behaviour of the fringes, and the reflected system was projected by means of a lens L_2 on to the slit of an autocollimating spectrograph having an 8 cm. reflecting grating. The light reflected from the latter entered two objectives O_1 and O_2, and fell on two photographic plates P_1 and P_2. In this way the two potassium doublets were photographed simultaneously.

To produce the hooks plane-parallel glass plates were inserted in the path of the beam passing through the glass tube, the various plates ranging in thickness from 1 mm. to 32 mm., so that a 1 mm. increase in thickness could be obtained from 1 mm. to 63 mm.

As the first doublet is fairly wide—34 Å—it was photographed in the first-order spectrum with a 2 minutes' exposure on the plate P_1. The violet doublet being narrow was photographed in the fourth-order spectrum with an exposure 1·5–2 minutes on the plate P_2.

For the red doublet a gelatine filter Wratten No. 29 F, transmitting up to 6100 Å, was placed in front of the plate to exclude the blue light scattered by the grating as well as the second-order ultra-violet light which partly overlapped the first-order red light. It was found that the filter caused no distortion of the dispersion image. Ilford Special Rapid plates, sensitized with dicyanine, were used and two series of photographs were made under the conditions described above, one series supplementing the other.

Metallic potassium was placed in a retort 2 cm. diameter and 8 cm. long, and this retort was inserted in the quartz tube. The gases evolved during heating were pumped away, the pressure being maintained at a few mms.

4. *Experimental Results.*

The results of the measurements made from the first series of photographs is given in Table I. Ten photographs were taken on each plate using the same heating current but with different thicknesses of plate inserted in the interferometer, so that one and the same quantity was computed from measurements made at different distances from the absorption lines. For the red doublet these distances were greater than 1 Å, but for the violet doublet they were seldom more than 1 Å, and at small densities were even less than 0·5 Å.

TABLE I.

Values of ρ_1.	$\left(\frac{\rho_1}{\rho_2}\right)_A$.	$\left(\frac{\rho_1}{\rho_2}\right)_B$.	σ.	Remarks.
2.10^{34}	2·001	1·986	94	Average from 5 photos.
3	2·011	1·977	101	„ „ 6 „
4	1·998	2·019	105	„ „ 4 „
6	1·975	2·114	101	„ „ 3 „
11	1·998	2·077	114	„ „ 3 „
21	2·022	2·053	111	„ „ 5 „
23	2·006	2·132	114	„ „ 4 „

As a rule not all of the photographs on a plate were suitable for measurements, the third group of cyanogen bands, beginning at 4216 Å, overlapping the second potassium doublet. The necessary quantities were measured and their average for each plate is given in the table. The first column gives the values of ρ_1 for the brighter line of the red doublet. It is practically proportional to the vapour density. The second column gives the ratio $\left(\frac{\rho_1}{\rho_2}\right)_A = \left(\frac{N_1}{N_2}\right)_A$ for the two lines of the red doublet, and the corresponding ratio for the violet doublet is given in the third column. The fourth column indicates the values of σ under consideration, *i. e.*,

$$\sigma = \frac{(N_1 + N_2)_A}{(N_1 + N_2)_B}.$$

These results show that the value of σ varied by 20 per cent. as the density of the vapour increased 12 times. No reliable measurements could be made at high densities as the vapour in the tube assumed a "prismatic" distribution at high temperatures, as stated by Wood*. Since the refractive index varies greatly in the neighbourhood of absorption lines, such a prismatic effect alters the lines of

* Phil. Mag. viii. p. 295 (1904).

equal inclination into lines of equal thickness, the lines are out of focus, and the hooks become partly diffused, sometimes vanishing altogether. It is possible that this effect accounts for the variation of σ, and in the second series of photographs the author endeavoured to test this statement. It appears that the results obtained by Bevan, Rogestwenski, and Baxter are affected by this prismatic effect, and therefore they are not as reliable as would be desired.

In the second series of photographs the retort aperture was diminished to 1 cm. so that the central portion of the vapour column was alone effective. With such a retort the vertical vapour-density distribution was more regular, and measurements were now possible at vapour densities twice as great as in the first series of measurements. The results obtained are given in Table II.

TABLE II.

Values of ρ_1.	$\left(\frac{\rho_1}{\rho_2}\right)_A$.	$\left(\frac{\rho_1}{\rho_2}\right)_B$.	σ.	Remarks.
16.10^{24}	1·995	2·036	110	Average from 4 photos.
37	1·983	1·989	111	„ „ 2 „
40	1·936	2·088	113	„ „ 5 „
45	1·960	2·054	111	„ „ 6 „

The values for σ approximate to 110, and they are not changed by a three-fold variation of ρ_1. This fact proves that the prismatic effect accounts for the values of this ratio. In order to avoid this effect the vapour tube and the interferometer system were then arranged in a vertical position.

The beam of light SL_1 (fig. 2) passed horizontally to the interferometer, and at J proceeded in a vertical direction to the level of the spectrograph slit, the spectrograph being situated in such a manner that the horizontal ray entered it from the interferometer. The interference fringes produced by the latter in the vertical position being vertical on the slit, they were rotated through 90° by means of a right-angled prism placed at an angle of 45° between the lens L_2 and the interferometer, the latter being firmly mounted on stone slabs. In order to eliminate air-convection currents in this position the box containing the two tubes was provided with double walls and was water-cooled, so that finally the fringes remained stationary. Observations of dispersion in sodium vapour near the yellow doublet showed that the prismatic vapour-density effect was completely eliminated. The vapour density could be varied over a much greater range, the fringes remaining sharp in all details.

The results obtained from this third series of photographs are given in Table III. As will be seen, the systematic variation in the values of σ are less than 10 per cent., *i. e.* it is half that found in the first series of results, although the vapour density varied over a range twice as great as was used in this first series.

TABLE III.

Values of ρ_1.	$\left(\frac{\rho_1}{\rho_2}\right)_A$.	$\left(\frac{\rho_1}{\rho_2}\right)_B$.	σ.	Remarks.
2.10^{24}	2·027	1·975	102	Average from 4 photos.
3	2·010	1·950	101	„ „ 5 „
4	2·003	2·015	101	„ „ 6 „
8	1·991	2·010	106	„ „ 4 „
11	2·022	2·110	107	„ „ 8 „
19	1·973	2·079	106	„ „ 6 „
23	2·008	2·115	111	„ „ 2 „
43	1·975	2·131	111	„ „ 3 „

The results quoted in Table III. are absolutely free from the prismatic distribution of vapour effect, and are therefore reliable. The variation in σ remained systematic, but was only half of that obtained in the previous case.

5. *Discussion of Results.*

It has been mentioned previously that measurements with the violet doublet have been made at small vapour densities and, in particular, for large path differences in regions very close to the absorption line; the absolute accuracy of the measurements was within 0·01 Å. The distances δ were less than 0·5 Å. From formula (7) it is obvious that then the relative error in the ratio $\frac{\rho_1}{\rho_2}$ for the violet doublet can be as high as 10–12 per cent., and the error for σ in this case is the same. Thus the low values for σ which were obtained from measurements at small densities coincide, within the limits of error, with the high values obtained from measurements at greater densities, and it is impossible to establish the dependence of σ on density. In order to make this possible it is necessary to make the measurements at small vapour densities and at greater distances of the hook from the absorption line.

The possibility of such a procedure is obvious from the formulæ (6) and (7). For the same density (a being proportional to ρ and accordingly also to N) the value of δ^2 is

proportional to d—the thickness of the vapour column. It follows therefore that if δ increases three-fold the vapour column is to be taken nine times as thick, *i. e.* 70 cm. instead of 8 cm., as in the present work. Investigations with such a long column are in progress.

In the preliminary measurements made by the author and Gamoff* the value for σ at low vapour densities reached 110, but on further decreasing the density, so that the hook-distances were less than 0·5 Å, the value of σ decreased as in previous cases. The simultaneous alteration of σ with decrease of δ becomes quite obvious, from which we can conclude with certainty that *the ratio σ does not vary with the density but does change with* δ; this relation between σ and the measured hook distances, however, is observable only in the immediate neighbourhood of the absorption lines. It has been pointed out by Rogestwenski† that a systematic deviation of the experimental dispersion curve from those drawn on the basis of theoretical considerations begins at a distance 0·5 Å from the absorption lines, and in such a case no measurements can be made within this distance.

It was therefore of interest to select from all the data given in the previous tables only those which for the violet doublet satisfied the condition $\delta > 0{\cdot}5$ Å. The values so selected are given in Table IV. and form a conclusive series.

In the last column average values for σ are given for each plate. All of them approximate to $\sigma = 110$, except the values 114 and 108, but the latter were obtained from plates with only one good photograph, so that the results for the three series are in close agreement and give $\sigma = 110$ at all vapour densities.

These results are certainly more accurate than those obtained by Bevan and Baxter, and the 20 per cent. to 50 per cent. greater value of these experimenters lies in the fact that they worked at great distances from the absorption lines outside the absorption bands which are always seen in the red end of the spectrum at high vapour density. Bevan‡ has pointed out that the discrepancy between the theoretical and experimental dispersion curves begins in the neighbourhood of the absorption band, so that measurements made at great distances from the absorption lines give values of σ affected by the red absorption band,

* The preliminary results were communicated at the 4th Physical Congress at Leningrad in Sept. 1924. These measurements were performed and will be published in another place.

† *Ann. d. Phys.* xxxix. p. 307 (1912).

‡ Proc. Roy. Soc. A, lxxxv. p. 58 (1911).

Table IV.

δ for the violet doublet in Å.	$\rho_1 \times 10^{24}$.	σ.	Average value of σ for plate.
	1st Series.		
0·62	21	112	
0·56	21	110	110
0·53	21	110	
0·50	21	106	
0·50	23	109	109
	2nd Series.		
0·63	37	111	
0·54	37	108	110
0·50	37	112	
0·68	45	109	
0·58	44	108	109
0·52	44	109	
0·56	43	110	111
0·50	42	113	
	3rd Series.		
0·57	11	114	114
0·52	17	108	108
0·71	24	114	
0·60	24	109	111
0·50	20	110	
0·67	30	113	
0·54	30	110	110
0·52	30	107	
0·70	42	107	
0·66	43	112	111
0·54	43	113	

although it is difficult to explain what these values really represent. In Miss Baxter's investigation the dispersion could not be measured near the absorption lines, and the dispersion curves were photographed only between the two doublets. The record is shown in fig. 3. Interference fringes BB are curved by the anomalous dispersion. They intersect the horizontal line AA which is the image of a wire in front of the spectrograph slit. Before the tube containing the potassium was heated, the interferometer was adjusted so that the horizontal zero fringe coincided

with the horizontal image. After heating was commenced a gradually increasing path difference was introduced by the vapour, this path difference depending on the wave-length and the dispersion. The fringes were displaced, and fig. 3 shows the pattern at a stationary temperature.

To estimate the path difference introduced for different wave-lengths we follow the horizontal line from the violet doublet and count the number of fringes intersected. Denoting by 1 the first fringe after the violet doublet and moving to the right, we mark the points 2, 3, etc. in the direction of the red doublet as far as it is possible to approach it. The wave-lengths corresponding to these points are found by comparison with the iron spectrum.

Fig. 3.

Let the nth point correspond to a wave-length λ, the number of intersected fringes being n. The path difference can be calculated from this number only when the first fringe is the real first following the zero one. As soon as dispersion sets in we are unable to trace the zero fringe unless it has been kept under observation during the whole process of heating. It is at a certain distance from our first fringe, above or below it. Therefore a certain unknown number, k, of fringes is introduced between the first and zero fringes. Our nth fringe becomes an $(n+k)$th fringe and the path difference for λ will be $(n+k)\lambda$.

This path difference can be determined in another way, if we consider everything that has been introduced in the interferometer paths. In the first place we have a column of a dispersing substance of thickness d. For such a substance the refractive index $n-1$ is a function of λ and $f(\lambda)$ is determined by

$$f(\lambda) = n-1 = \frac{a_1\lambda^2}{2(\lambda^2-\lambda_1^2)} + \frac{a_2\lambda^2}{2(\lambda^2-\lambda_2^2)}.$$

Such a column of vapour gives a path difference $f(\lambda)d$. In addition, the zero fringe may have moved during the

experiment from the horizontal line AA, *i. e.* a path difference Δ independent of the vapour might have been created. In such a case

$$(n+k)\lambda = f(\lambda)d + \Delta$$

or

$$(n+k) = \frac{a'\lambda}{\lambda^2-\lambda_1^2} + \frac{a''\lambda}{\lambda^2-\lambda_2^2} + \frac{\Delta}{\lambda}, \quad . \quad . \quad (10)$$

where a' and a'' are constants proportional to the number of absorbing centres of the first and second doublets. The ratio $\frac{a'}{a''}$ has to be found by means of equation (10).

In moving along the horizontal line we take several points and must therefore write for each photograph a series of equations similar to (10).

The number n is counted and λ measured, so that for each temperature a system of equations similar to (10) is found with the four unknown quantities k, a', a'', and Δ. The number of equations is greater than the number of unknown quantities. In some cases as many as 40 points have been measured.

If the zero fringe remains undisplaced during the experiment, as can be seen from its position after the tube has cooled, the value of Δ is zero and

$$n+k = \frac{a'\lambda}{\lambda^2-\lambda_1^2} + \frac{a''\lambda}{\lambda^2-\lambda_2^2}. \quad . \quad . \quad . \quad . \quad (11)$$

This differs fundamentally from that proposed by Miss Baxter, viz.,

$$n = \frac{a'\lambda}{\lambda^2-\lambda_1^2} + \frac{a''\lambda}{\lambda^2-\lambda_2^2} + \frac{k}{\lambda}.$$

The solution of equation (11) gives the following values:—

Table V.

Curve.	$\frac{a'}{a''}$.	σ.	T° C.
2	550	152	316
3	570	158	327
4	607	168	340
5	383	106	365
6	576	160	376
7	510	141	385

The result shown in Table V. is the reverse of that

obtained by Miss Baxter; the ratio of the constants of the two doublets does not depend upon vapour density, the variation of σ being irregular. Curve 5 is the only one which differs from the rest. This shows that the correction term Δ cannot be neglected in every case. Accordingly a complete system of equations has been solved for several curves and the result is a nearly constant value for σ, the variation being quite irregular within the limits 120 to 140. The average value of the ratio is 130 so that a six-fold change of vapour density does not affect this ratio, but the value of σ obtained is not exactly the relation between the numbers of electrons corresponding to the red and violet doublets. The effect of the red absorption band makes the ratio greater than the value 110 found in the present work.

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XCIX. *On the Determination of the Power-Voltage characteristic of a Siemens Ozonizer.* *By* R. Winstanley Lunt, *M.Sc., Ph.D.**

IN experiments on the chemical changes arising from the ionization by collision produced in a gas when subjected to single-phase alternating electric fields applied by means of a Siemens Ozonizer, it is frequently necessary to determine the power consumed in the ionized gas. The power to be determined is of the order of 10–50 watts for ozonisers of laboratory dimensions operated in the range of commercial frequencies. There are five methods available for the measurement of this power. The power may be determined by a direct thermal method; for example, by observing the temperature changes which take place in water-streams of known magnitude which cool the ozonizer electrodes; or by employing a Duddell oscillograph, or a cathode-ray oscillograph, or a high-tension electrostatic wattmeter; and, lastly, by using a low-tension dynamometer wattmeter. Investigations in this laboratory have shown the first method to be unsatisfactory when applied to ozonizers of laboratory dimensions in the range of commercial frequencies. Errors arise from the difficulty of achieving good thermal insulation, and of avoiding the heating of the stream of cooling water by leakage currents.

* Communicated by Prof. F. G. Donnan, F.R.S.

Although the instruments employed in the second, third, and fourth methods are capable of giving accurate measurements over a wide range of frequency, they are costly and involve an elaborate technique. The fifth method has been introduced recently by Becker *. It has the advantage that such an instrument is relatively inexpensive, and simple in use. The description of the method given by Becker is somewhat meagre; in addition, the corrections applied and the precautions enumerated would appear to be inadequate. In this communication an attempt has been made to give a more complete analysis of the factors involved in the method, together with a description of the appropriate technique.

It is convenient to consider in the first place the simple case of an ozonizer the electrodes of which are not water-cooled. A wattmeter is introduced into the primary circuit so that it reads the power absorbed by the transformer, to the secondary of which the ozonizer is connected. A voltmeter, preferably of the electrostatic type, is connected in parallel with the ozonizer between the high-tension line and earth; and a milliameter is connected between the earth and the low-tension secondary terminal of the transformer in order to record the total secondary current. A second milliameter, connected between the low-tension electrode of the ozonizer and earth, indicates the current flowing through the ozonizer. For frequencies above the maximum rated frequency of a dynamometer wattmeter, the correction for errors due to frequency is cited in a chart which can be provided by the instrument makers. Alternatively, at any given frequency the inductive effect of the current and volt coils may be compensated by introducing in series with each coil a capacity of reactance equal and opposite to that of the coil, but the error due to eddy currents remains.

Let V denote a secondary voltage such that a discharge takes place in the gas in the ozonizer; and let W' and i' denote, respectively, the corresponding values of the power absorbed by the transformer and of the total secondary current. And let W'' denote the power absorbed by the transformer at the frequency at which W' has been measured, and corresponding to the same line voltage V and to a total secondary current i'', when no discharge takes place in the gas. This condition can be achieved most readily by evacuating the annular space to a pressure of 10^{-3}–10^{-4} mm. Hg; or alternatively by increasing the pressure of the gas

* Becker, *Wiss. Ver. des Siemens Konzerns* (1921).

until no luminous discharge takes place, for which purpose a gas of high dielectric strength is naturally to be preferred. W′ is the sum of the following quantities : the magnetic loss of the transformer, which is solely a function of the secondary voltage V at constant frequency ; the copper loss of the transformer, which is solely a function of the total secondary current i' at constant frequency ; the corona loss, which includes any external surface loss between the electrodes of the ozonizer and any dielectric loss in the ozonizer*, and which is solely a function of the line voltage V at any given frequency ; and of the power W_v expended in the ionized gas. Similarly, W″ is the sum of the magnetic and corona losses corresponding to the line voltage V and of the copper loss corresponding to the total secondary current i''. Let W_{2_i} denote the copper loss of the transformer at the frequency at which W′ and W″ have been determined, corresponding to a total secondary current i. Then the power developed in the ionized gas corresponding to the line voltage V is given by

$$\begin{aligned} W_v &= (W' - W_{2_{i'}}) - (W'' - W_{2_{i''}}) \\ &= W' - W'' - W_{2_{i'}} + W_{2_{i''}}. \end{aligned}$$

With an accurate wattmeter reading to $\pm \frac{1}{4}$ per cent. it is readily possible thus to determine W_v within 1 per cent. when using ozonizers of laboratory dimensions in the range of commercial frequencies, for it has been found in practice that W_v ranges from approximately 10 to 30 per cent. of W′.

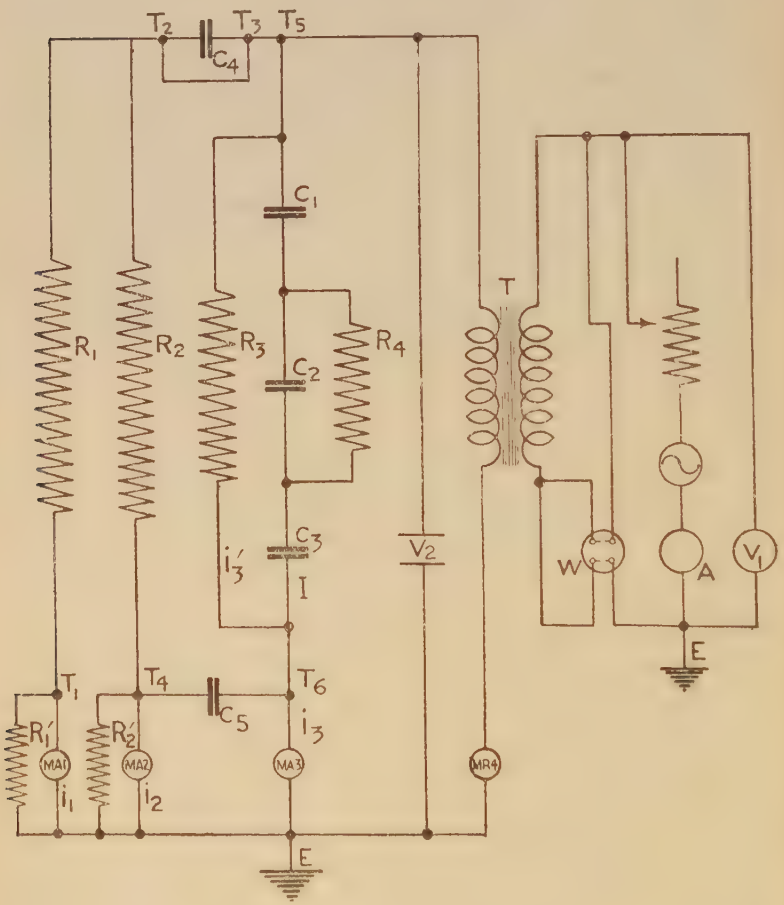
The copper loss of the transformer, W_2, as a function of the secondary current may be determined, at any constant frequency, over the range of permissible secondary current (as given by the transformer rating) from measurements of the power absorbed by the primary when the secondary is short-circuited through a milliammeter. It may be noted that the primary voltage necessary is very small.

The general expression for W_v, including the case in which the electrodes are cooled by water streams, may now be developed. The general circuit is represented in the accompanying diagram, where V_2 denotes the high-tension voltmeter measuring the potential applied to the ozonizer, the walls and annular space of which are associated with the capacities C_1, C_3, and C_2 respectively †. R_3 and R_4

* The dielectric loss in glass and silica is exceedingly small at commercial frequencies.

† *Cf.* Phil. Mag. xlix. p. 1232 (1925).

represent, respectively, the inverse of the conductivity due to gaseous ions in the annular space, and the inverse of the total equivalent conductivity corresponding to the surface leakage between the ozonizer electrodes T_5 and T_6, and to



the dielectric loss in the material forming the walls of the ozonizer. The wattmeter is represented by W, and the milliammeters reading the ozonizer current and the total secondary current are denoted by MA 3 and MA 4 respectively.

It will be convenient to describe firstly the technique appropriate to the use of water-cooled electrodes. The water stream cooling the high-tension electrode T_5, carried preferably in glass tubing, must be carefully insulated for the applied secondary voltage in order to stabilise and to facilitate the measurement of the currents flowing in this water stream. In order to measure the current flowing in this water column from T_5 towards the tap supplying the water, an insulated copper tube, the connexion to which is denoted by T_1, is introduced in the water stream between the tap and the vessel cooling the high-tension electrode. It is connected to earth through the milliammeter MA 1. The length of the water column between the tap, which must be considered as connected to earth, and this copper tube is adjusted so that the resistance of this water column, denoted by R_1', is very much greater than that of the milliammeter. No sensible fraction of the current flowing from the high-tension electrode T_5 towards the tap will then flow in the water column between the copper tube and the tap; and the milliameter MA 1 will therefore read the current flowing in the water column between T_5 and this copper tube, the resistance of which is denoted by R_1. The stream of water flowing from the tap to the cooling vessel associated with the high-tension electrode is thus represented by the resistances R_1 and R_1'. The use of a silica or glass cooling vessel, which is immersed in or placed adjacent to the high-tension electrode, introduces a capacity denoted by C_4. Current flowing from this electrode along the water column to the tap must therefore flow through C_4 and R_1 in series. The capacity C_4 is eliminated by the method described in a previous communication, in which copper tubes, the connexions to which are represented by T_2 and T_3, are inserted in the water stream at both inlet to and outlet from this cooling vessel *. These are connected to the high-tension electrode. From the vessel cooling this electrode the water stream is led through a further length of tubing, preferably of glass, insulated for the applied secondary voltage to another insulated copper tube, the connexion to which is denoted by T_4, and thence to waste directly, or after passing through the vessel cooling the low-tension electrode T_6, thereby introducing the capacity represented by C_5. The water stream must be considered as again connected to earth, where it flows to waste. In order to measure the current flowing through the water column

* Phil. Mag. ii. p. 314 (1926).

between T_3 and T_4, the resistance of which is denoted by R_2, it is therefore necessary to connect T_4 to earth through the milliammeter MA 2, and to provide that the resistance of the water column between T_4 and waste, which is denoted by R_2', is very much greater than that of the milliameter. The lengths and cross-sections of these water columns must be adjusted so that the currents carried by R_1 and R_2 are conveniently low.

In the general case the power W_v', indicated by the wattmeter and corresponding at a given frequency f to a line voltage V and to a total secondary current i, is the sum of the losses previously enumerated and of W_4, the losses associated with the stream of water cooling the high-tension electrode at the voltage V. W_v' is therefore given by

$$W_v' = W_v + W_1 + W_{2i} + W_3 + W_4,$$

where W_1 and W_3 denote respectively the magnetic loss and the corona loss corresponding to the line voltage V, and where, as before, it is presupposed that W_1, W_2, W_3, and W_4 refer to the same frequency, f, as that at which W_v' has been determined.

$$W_v = W_v' - (W_1 + W_{2i} + W_3 + W_4),$$

from which equation W_v may readily be calculated.

The magnetic or hysteresis loss of the transformer W_1 may be determined at any frequency as a function of V from observations of the power absorbed by the transformer when the secondary is open-circuited but connected across the electrostatic voltmeter V_2.

The corona loss W_3 may be determined at any frequency as a function of V by disconnecting the water cooling system and observing the wattmeter reading W_3' when no discharge takes place in the gas in the ozonizer. If i is the value of the total secondary current corresponding to the line voltage V, then W_3, corresponding to the same voltage V, is given by

$$W_3 = W_3' - (W_1 + W_{2i}),$$

where it is presupposed that W_1 and W_2 refer to the frequency f at which W_3' has been determined.

It has already been stated that, so determined, W_3 includes any external surface loss between the electrodes and any dielectric loss in the walls of the ozonizer. Such losses

would correspond to a resistance term in parallel with the capacities C_1, C_2, and C_3; it is represented in the diagram by R_3 corresponding to a line voltage V at a frequency f. The current i_3', flowing through the R_3, is given by $\frac{V}{R_3}$; and the current, i_3, read by the milliammeter MA_3, is the vector sum of i_3' and I, the current flowing through the system comprising C_1, C_2, C_3, and R_4. By designing the ozonizer so that the insulation resistance between the electrodes is very great, and by making the vessel of silica or of a glass of very low dielectric loss, the ratio $\frac{V}{R_3}$ can be made negligibly small compared with I or i_3, and the error arising from i_3' therefore vanishes.

The loss in the cooling water W_4 due to the currents flowing in R_1 and R_2 may be evacuated in two ways. The cooling-water system is connected to the high tension electrode of the ozonizer in the manner previously described. The first method consists in calculating W_4 from simultaneous measurements at any given frequency f of the secondary voltage V, the total secondary current i, and of the power W_4' absorbed by the transformer when no discharge takes place in the gas in the ozonizer.

Then W_4 is given by

$$W_4 = W_4' - (W_1 + W_{2i} + W_3),$$

where it is presupposed that W_1, W_2, and W_3 refer to the frequency f and the voltage V at which W_4' has been measured. In the second method the power is computed from the secondary voltage V and the corresponding values of the currents i_1, i_2 flowing through the resistances R_1 and R_2. W_4 is then given by $W_4 = V(i_1 + i_2)$. The variable conductivity of tap-water necessitates the determination of W_4 before. and after, any determination of the total power W′ supplied to the transformer when a discharge is taking place through the gas in the ozonizer.

In conclusion, the author wishes to record his indebtedness to Mr. G. A. Elliott, M.Sc., for many suggestions in the development of the above technique.

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C. *The Freezing-Points of Concentrated Solutions.*—Part I. *Experimental Methods and the Freezing-Points of Potassium Chloride Solutions.* *By* Edward Richard Jones *and* Charles R. Bury *.

THE work described here was undertaken with the object of testing experimental methods: potassium chloride solutions were chosen as the subject of investigation because their freezing points have probably been studied more fully than those of any other substance. (A list of previous work is given by Randall and White, J. A. C. S. 1926, xlviii. p. 2515.) Comparison of activities calculated from our own and from other freezing-point determinations with those calculated from the E.M.F. of concentration cells indicate that our measurements are more reliable than those of previous workers.

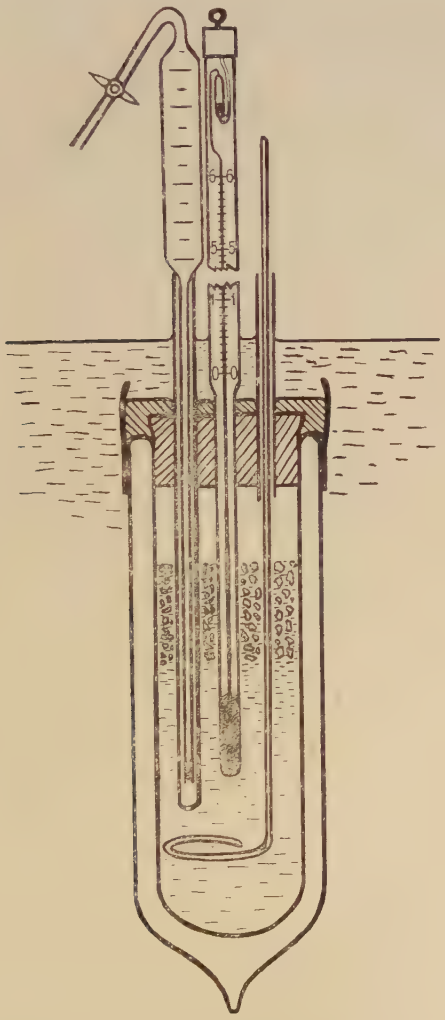
The method of Adams (J. A. C. S. 1915, xxxvii. (1), p. 481), which is essentially a modification of the equilibrium method of Roloff (*Zeit. phys. Chem.* 1895, xviii. p. 572), consists in determining the temperature and the composition of a solution in equilibrium with ice, these being enclosed in a Dewar flask surrounded by ice. With dilute solutions, the temperature inside the flask differs only slightly from that outside; the heat transfer is therefore negligible, and the method is capable of giving very accurate results. With concentrated solutions, the freezing-points of which are lower, the heat transfer is not negligible; equilibrium is never reached, and the temperatures obtained are higher than the true freezing-points. Rodebush (J. A. C. S. 1918, xl. (2), p. 1204) has employed the method with concentrated solutions, and his results are among the most accurate yet recorded, but it is obvious from his description that equilibrium was not obtained. We find the recorded temperature is dependent on that of the outside bath, but providing these do not differ by more than half a degree, the effect is within the limits of our experimental error. Instead of having the flask surrounded by ice, we found it desirable to sink it in a brine bath, the temperature of which was kept within 0°·1 C. of that of the freezing-point of the solution, and the increased accuracy of our results is due to this small modification.

Temperatures were measured by a Beckmann thermometer standardized to 0°·005 by the National Physical Laboratory: its pressure coefficient was found to be practically negligible (0·0024 degrees/cm. mercury), and all readings were corrected for emergent stem. Adams and Rodebush used

* Communicated by the Authors.

multiple-junction thermoelements: with concentrated solutions, however, great sensitivity is not essential, and since the thermoelement used by Rodebush could only be standardized

Fig. 1.



to the nearest 0°·01 by the Bureau of Standards, his temperature measurements could not be as accurate as ours. The greatest disadvantage of the Beckmann thermometer is its rather limited range.

The apparatus (fig. 1) consisted of a Dewar flask of 400 c.c.

capacity, closed by a rubber bung through which passed the thermometer, a stirrer, a closed tube for holding a pipette in order that the latter might attain the temperature of the solution, and two tubes, not shown in the figure. One of these was used for the withdrawal of samples of solution in the pipette, and the other for the addition of a concentrated solution of the solute. To avoid the introduction of warm air during stirring, a current of pure air was passed through a coil in the outer bath and into the flask through this tube. The flask was sunk in a vigorously stirred brine bath, the temperature of which was measured by a second Beckmann thermometer, and was kept within $0^{\circ}{\cdot}1$ of that inside the flask by addition of ice or salt.

In preliminary experiments, some inconsistent results were traced to leakage of brine into the flask. This was prevented by a mercury seal: a short length of rubber tubing, part of the inner tube of a motor tyre, was slipped over the top of the flask, and into this was poured sufficient mercury to cover the bung to a depth of 1 cm. Further, a quantity of ammonium sulphate was added to the brine, and samples withdrawn from the flask were tested for the presence of sulphate; none was ever found after the mercury seal had been adopted.

After filling the flask to within about two inches of the top with distilled water and finely crushed ice, prepared from distilled water, the apparatus was assembled, and the temperature of the outer bath adjusted. The apparatus was allowed to stand for half an hour: on gently stirring, equilibrium was rapidly attained, after which the temperature remained constant. After another half-hour, the freezing-point of the pure solvent was noted and a small quantity of a previously cooled concentrated solution of potassium chloride added. The solution was stirred vigorously for a short time to ensure complete mixture, and the bath temperature adjusted to that of the freezing-point of the solution: with occasional gentle stirring the temperature then remained constant for hours. The temperature was independent of the rate of stirring providing this was gentle—continuous and vigorous stirring melted the ice, and caused a steady rise of temperature and fall in concentration. After about an hour, a sample of the solution was withdrawn by means of the pipette, the tip of which contained a plug of glass wool. A further portion of potassium chloride was added, and the freezing-point of a more concentrated solution determined, and so on.

The solution withdrawn was divided into three portions: one portion was tested for the presence of sulphate, and the other two were analysed by titration with silver nitrate, using Mohr's method. The amount of solution withdrawn

for analysis varied with its concentration, sufficient being taken to require about 40 c.c. of tenth normal silver nitrate. The difference between the duplicate analyses was usually less than one part in a thousand ; when greater than 1 in 500, the results were neglected. The silver nitrate solution was standardized by means of pure potassium chloride.

With this method, the error due to equilibrium not being established is avoided : the only errors are those involved in the measurement of the temperature and of the concentration. In our most dilute solutions the former predominates, but with the more concentrated solutions the error in temperature measurement is negligible in comparison with the analytical error, which remains constant throughout.

The potassium chloride was recrystallized four times from distilled water, the mother liquor after each crystallization being removed in a centrifuge. The samples used for standardizing the silver nitrate solution were dried at a dull red heat in a platinum crucible.

TABLE I.

m.	θ.	γ'.	m.	θ.	γ'.
0·0988	0·340	0·778	0·8303	2·719	0·609
0·1205	0·412	0·762	0·9182	3·001	0·601
0·1246	0·425	0·759	1·020	3·328	0·593
0·1816	0·616	0·733	1·112	3·618	0·585
0·2381	0·803	0·712	1·220	3·960	0·577
0·2710	0·913	0·703	1·304	4·230	0·572
0·2998	1·007	0·694	1·397	4·528	0·567
0·4042	1·347	0·669	1·484	4·804	0·563
0·4549	1·511	0·659	1·608	5·208	0·558
0·5204	1·723	0·648	1·615	5·223	0·557
0·6047	1·992	0·635	1·704	5·519	0·554
0·7013	2·303	0·623	1·778	5·757	0·551
0·7856	2·577	0·614	1·818	5·882	0·550

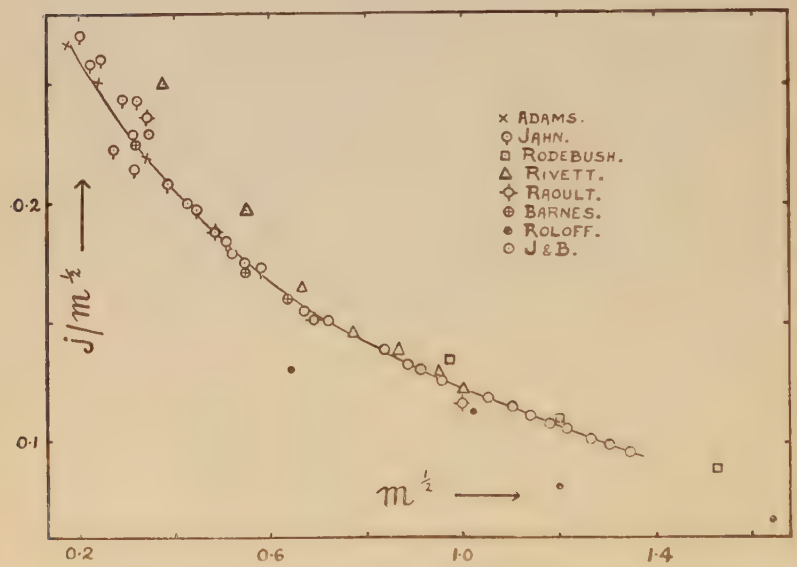
The results obtained are given in Table I. In the first column are given the concentrations of the solutions in mols. per 1000 grams of water (m) ; in the second, the depressions of the freezing-point of water (θ) ; and in the third, the activity coefficients (γ') calculated from the equation of Lewis and Randall ('Thermodynamics and the Free Energy of Chemical Substances,' McGraw-Hill Book Co., New York, 1923, Chap. XXVII.) :

$$\log_e \gamma' = \int_0^m -j\,d\log_e m - j + 0{\cdot}000285 \int_0^m \frac{\theta}{m}\,d\theta,$$

where $$j = 1 - \frac{\theta}{3{\cdot}716\,m}.$$

The integrals have been evaluated graphically, the method of Randall (J. A. C. S. 1926, xlviii. p. 2512) being used for the first integral. The results of Adams (*loc. cit.*) have been used to draw the curves for dilute solutions.

Fig. 2.



Our results are compared graphically with those of previous workers at these concentrations in fig. 2, in which $j/m^{\frac{1}{2}}$ is plotted against $m^{\frac{1}{2}}$. This graph has been used in the evaluation

Table II.

	γ'.				γ.		
m.	J. & B.	L. & R.	$L_{1(298)}$.	$\bar{C}_{p_1}-\bar{C}^{\circ}_{p_1}$.	J. & B.	L. & R.	N. & M.
0·05	0·824	0·839	0·03	−0·002	0·842	0·857	0·841
0·10	0·777	0·791	0·05	−0·004	0·797	0·811	0·796
0·20	0·726	0·737	0·13	−0·010	0·749	0·760	0·749
0·35	0·680		0·33	−0·021	0·706		
0·50	0·651	0·660	0·66	−0·035	0·680	0·689	0·682
0·75	0·617		1·37	−0·065	0·650		
1·00	0·594		2·59	−0·103	0·632		0·634
1·25	0·574		4·14	−0·150	0·617		
1·50	0·561		5·90	−0·208	0·609		
1·80	0·550		8·26	−0·286	0·605		

of activities; it is very susceptible to experimental errors, and therefore lends itself to graphical comparison of closely agreeing data.

In Table II., values of the activity coefficients at round concentrations, obtained by interpolation from the data in Table I., are compared with the figures given by Lewis and Randall (*op. cit.* p. 363) based on all previous determinations. These "preliminary" activity coefficients are valid only at the freezing-points; from these we have calculated the activity coefficients at 25° C. (γ) from Lewis and Randall's equation (*op. cit.* p. 350). We have used the data of Wüst and Lange (*Zeit. phys. Chem.* 1925, cxvi. p. 161) for the partial molal heat content of the solvent (L_1), and the partial molal heat capacities, $(\overline{C}_{p_1} - C^0_{p_1})$, have been deduced from the data of Richards and Lowe (J. A. C. S. 1921, xliii. (1) p. 770). In the last column of Table II. are given the activity coefficients of potassium chloride deduced by Lewis and Randall (*op. cit.* p. 360) from measurements at 25° C. of the E.M.F. of cells containing potassium-chloride solutions by Noyes and MacInnes. Our corrected activity coefficients agree satisfactorily with these; the differences are within the possible errors of the graphical methods of integration used.

One of us (E. R. J.) acknowledges his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant during the Session 1925–26, and to the University of Wales for a Postgraduate Studentship during the Session 1926–27.

Edward Davies Chemical Laboratories,
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February 19th, 1927.

CI. *The Crystal Structure of Benzil.*

By Natalie C. B. Allen, *M.Sc.**

Formula. $C_6H_5CO \cdot CO\ C_6H_5$; molecular weight 210·1.

Crystallographic data.—Benzil belongs to the trigonal trapezohedral class (rhombohedral enantiomorphy). Groth (*Chemische Kristallographie*, vol. v. p. 200) gives the following data concerning it:—

$\alpha = 78° 13'$.

$a : c = 1 : 1{\cdot}6322$ (Martin, *N. Jahrb. f. Min. usw.* (1891), Beil. vii. p. 30).

* Communicated by Sir W. H. Bragg, K.B.E., F.R.S.

Specific gravity: 1·23 (Des Cloizeaux, *C. R.* lxviii. p. 308 (1869)).

Cleavage: {111} (good); $\{2\bar{1}\bar{1}\}$ and $\{10\bar{1}\}$ (poor).
Optical rotation: 25° (±0°·3) per mm. for $\lambda = 0{\cdot}5893$ (Des Cloizeaux, *loc. cit.*).

X-ray data.—Preliminary measurements made with a Bragg ionization spectrometer (molybdenum anticathode) gave

$$d_{10\bar{1}}\,(d_{11\bar{2}0}) = 4{\cdot}19\ \text{Å}.$$
$$d_{111}\,(d_{0001}) = 4{\cdot}58$$
$$d_{2\bar{1}\bar{1}}\,(d_{10\bar{1}0}) = 7{\cdot}28$$
$$d_{100}\,(d_{1\bar{0}\bar{1}}) = 6{\cdot}42$$

The first two of these spacings are in agreement with a

TABLE 1.

Rhombohedral lattice. $\alpha = 78°\ 8'$ *. 1 molecule/cell.		Spacing observed.	Hexagonal lattice. $a:c = 1:1{\cdot}6322$. 3 molecules/cell.	
Plane.	Spacing.		Spacing.	Plane.
111	4·58	4·58	13·75	0001
$2\bar{1}\bar{1}$	2·43	7·28	7·30	$10\bar{1}0$
$10\bar{1}$	4·21	4·19	4·21	$11\bar{2}0$
$41\bar{5}$	·92	2·72	2·76	$12\bar{3}0$
$5\bar{1}\bar{1}$	1·17	3·52	3·53	$20\bar{2}1$
$1\bar{1}\bar{1}$	3·53	3·52	3·53	$20\bar{2}\bar{1}$
$8\bar{1}\bar{1}$	·76	2·29	2·29	$30\bar{3}2$
$4\bar{5}\bar{5}$	·76	2·29	2·29	$30\bar{3}\bar{2}$
100	6·44	6·42	6·44	$10\bar{1}\bar{1}$
$1\bar{2}\bar{2}$	2·15	6·42	6·44	$10\bar{1}1$
411	1·67	5·00	5·00	$10\bar{1}2$
$0\bar{1}\bar{1}$	5·00	5·00	5·00	$10\bar{1}\bar{2}$
$5\bar{2}\bar{2}$	1·29	3·87	3·88	$10\bar{1}3$
$1\bar{4}\bar{4}$	1·29	3·87	3·88	$10\bar{1}\bar{3}$
211	3·11	3·10	3·11	$10\bar{1}4$
$2\bar{5}\bar{5}$	1·04	3·10	3·11	$10\bar{1}\bar{4}$
$41\bar{2}$	1·34	4·02	4·03	$11\bar{2}1$
$2\bar{1}\bar{4}$	1·34	4·02	4·03	$11\bar{2}\bar{1}$
$52\bar{1}$	1·20	3·60	3·60	$11\bar{2}2$
$1\bar{2}\bar{5}$	1·20	3·60	3·60	$11\bar{2}\bar{2}$

* This value of α is calculated from $a:c = 1:1{\cdot}6322$.

rhombohedral cell containing *one* molecule, which would, therefore, possess six-fold symmetry. This is highly improbable, and examination of Table I. shows that, in fact, the rhombohedral cell gives some spacings which are not reconcilable with the actual measurements. On the other hand, a hexagonal cell containing *three* molecules gives calculated spacings which show excellent agreement with those observed. No measured spacing is a multiple of that calculated on the basis of the hexagonal lattice, while only one is a sub-multiple. The (0001) plane gave only a third order reflexion, showing that the principal axis is a triad screw axis. The crystal, therefore, belongs to one of the space-groups D_3^3 (or D_3^5) or D_3^4 (or D_3^6) (Astbury and Yardley, Phil. Trans. Roy. Soc. A, ccxxiv. p. 249 (1924)). The spacing of any given plane is the same for all these space-groups; in order to distinguish between them it is necessary to compare the intensities of the reflexions from certain planes.

TABLE II.

Plane.	Observed intensity.
0001	—
0002	—
0003	Weak.
$10\bar{1}0$	Strong.
$20\bar{2}0$	Strong [$>(10\bar{1}0)$].
$30\bar{3}0$	Too weak to measure.
$40\bar{4}0$	Moderate.
$11\bar{2}0$	Strong.
$22\bar{4}0$	Weak.
$21\bar{3}0$	Moderate.
($mm\bar{2}ml$) zone.	
$11\bar{2}1$	Weak.
$11\bar{2}\bar{1}$	Weak.
$11\bar{2}2$	Weak.
$11\bar{2}\bar{2}$	Weak.
($m0\bar{m}l$) zone.	
$20\bar{2}1$	Strong.
$20\bar{2}\bar{1}$	Strong [$<(20\bar{2}1)$].
$30\bar{3}2$	Moderate.
$30\bar{3}\bar{2}$	Moderate.
$10\bar{1}1$	Too weak to measure.
$10\bar{1}\bar{1}$	Moderate.
$20\bar{2}2$	Moderately strong.
$30\bar{3}3$	Moderate.
$10\bar{1}2$	Strong.
$10\bar{1}\bar{2}$	Strong [$<(10\bar{1}2)$].
$10\bar{1}3$	Moderate.
$10\bar{1}\bar{3}$	Not found.
$10\bar{1}4$	Moderate.
$10\bar{1}\bar{4}$	Not found.

Table II. shows that the observed intensities of the reflexions from ($m0\bar{m}l$) and ($m0\bar{m}\bar{l}$) were different, while those from ($mm2\bar{m}l$ and ($mm2\bar{m}\bar{l}$) were the same. It follows that the dyad axes in the crystal are perpendicular to the $\{11\bar{2}0\}$ planes, and that the crystal therefore belongs to

the space-group D_3^4 (or D_3^6). These two space-groups differ from each other only in having trigonal screw axes of opposite rotations, that is, they represent enantiomorphous forms. The space-group found for the crystal is in agreement with the fact that it is optically active: in fact, benzil and quartz (Sir W. H. Bragg and R. E. Gibbs, Proc. Roy. Soc. A, cix. p. 405 (1925)) crystallize in the same space-group. The unit cell, like that of quartz, contains three molecules each possessing a dyad axis. It is interesting to notice that the optical activity of crystalline benzil is rather greater than that of quartz. Des Cloizeaux (*loc. cit.*) found, using Na light, that 1 mm. benzil was equivalent in rotatory power to 1·15 mm. quartz. This power of rotating the plane of polarization of light is evidently due simply to the spiral arrangement of the molecules and not to the arrangement of atoms within the molecule.

The axial lengths calculated for the above cell are $a=8{\cdot}42$ Å.; $c=13{\cdot}75$ Å.

Becker and Rose (*Z. f. Physik*, xiv. p. 369 (1923)), claim to have found by the rotating crystal method that $a=8{\cdot}15$ Å., $c=13{\cdot}46$ Å., and quote 1·38 as the specific gravity of benzil, without, however, giving references to the source of this value. The specific gravity as measured by Des Cloizeaux (1·23) was verified during the course of the present work, and the axial lengths given by Becker and Rose are quite out of agreement with this correct value.

The work was carried out at the Davy Faraday Laboratory of the Royal Institution, and acknowledgement is due to the Department of Scientific and Industrial Research for the necessary apparatus. The author would also like to express her thanks to Sir William Bragg, who suggested the work and gave much help during its progress.

Summary.

Benzil, in the crystalline state, belongs to the trigonal trapezohedral class. It is built upon a hexagonal lattice and the unit cell contains three molecules, which are disposed spirally about the principal axis. The molecule of benzil has a dyad axis and the space-group is D_3^4 (or D_3^6), the same as that of quartz. The optical activity, which slightly exceeds that of quartz, is due, as it is in quartz, to the arrangement of the molecules in the cell.

CII. *The Use of Gasfilled Photoelectric Cells.* *By* N. R. Campbell. (Communication from the Staff of the Research Laboratories of the General Electric Company, Ltd., Wembley.)

Summary.

Four methods of using gasfilled photoelectric cells, believed to be new, have been suggested by the study of the characteristics of these cells described in a recent paper.

(1) The response of the cell used in the ordinary manner to a given change of illumination can be considerably increased by applying to the cell a constant "priming" illumination from an independent source. This method is useful with "plane" cells exposed to moderate illuminations.

(2) The well-known method in which the photoelectric current is passed through a high resistance, the potential difference at the ends of which is measured, can be improved by using a thermionic current limiter in place of an ohmic resistance. There is some gain in the substitution even when the cell is used on the Townsend portion of the characteristic; but the gain is very much greater if it is used on a suitable unstable portion of the characteristic. The method is suitable for "spherical" cells when the range of illumination measured is not too great. It can be made very sensitive and used to detect illuminations which are beyond the range of an ordinary galvanometer used on the stable characteristic.

(3) The third and fourth methods are based on the change of frequency of the oscillations on the unstable part of the discharge when the illumination is changed. In the third method a part of the characteristic is used near the sparking potential which terminates the Townsend discharge. It is extremely sensitive and convenient; it can detect a candle at 1 km. distance without any elaborate or sensitive apparatus. "Spherical" cells must be used. The method may have applications in astronomy.

(4) The fourth method uses a similar change of frequency with illumination in the region where the unstable portion passes into the stable glow discharge. "Plane" cells must be used. The method may find an application in picture telegraphy.

In a recent paper to which frequent reference will be made*, attention was drawn to the variation of the form of the current-voltage characteristic of a gasfilled photoelectric

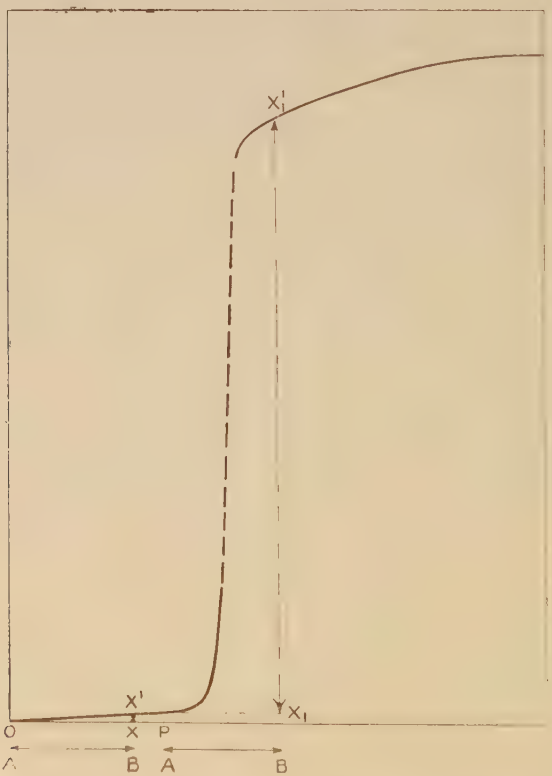
* Phil. Mag., April 1927, p. 944.

cell with the illumination incident upon it. An account will now be given of some methods of using such cells for the detection or measurement of light, which depend on the facts there described and have considerable advantages for some purposes over the methods in common use. Four of these methods will be distinguished.

The First Method. Moderate Illuminations.

The first is very simple and depends on the form of the curve (fig. 3 of the previous paper) relating current and illumination when the voltage applied to the cell is just

Fig. 1.



below the stopping potential; this curve is reproduced here in fig. 1. Suppose that we desire to obtain the greatest possible increase in current for a given increase of illumination represented by the length AB on the horizontal axis.

If we apply the increase of illumination to the unilluminated cell, the increase in current we shall obtain is XX^1. If, on the other hand, the same increase is applied when the illumination on the cell is already that represented by OP, the increase in current we shall obtain is $X_1X_1^1$, and is very much greater*.

The comparison exaggerates slightly the practical gain by this method; for, if the greatest illumination ever to be applied to the cell were OX, a current somewhat greater than XX^1 might be obtained without priming by increasing the voltage on the cell. But even when allowance is made for this possibility, considerable gains, *e.g.* a factor of 20, are obtained by priming with a suitable constant illumination. The method is only useful with "plane" cells (cf. *loc. cit.*); the priming illumination required for spherical cells would be too large compared with any illumination to the detection of which the method is likely to be applied.

The Second Method. Small Illuminations.

The second method is similar in principle to one in common use. When valve amplification is to be employed, it is usual to insert a high resistance in series with the cell and to apply the potential difference between its ends to the amplifier. Proposals have been made† to use a thermionic current limiter in place of the high resistance, mainly because it is easy by this method to obtain an equivalent to a resistance of any magnitude. There is also the advantage that, for a given mean current, the change of potential corresponding to a given change of illumination is greater when the thermionic valve is used. For when an ohmic resistance is used, the change from the characteristic for one illumination to that for another takes place along a straight line inclined to the potential axis, while, when the valve is used, it takes place along a line parallel to that axis. Again, though it is possible by this method to increase without limit the voltage change corresponding to a given light by using a sufficiently high resistance, in practice a limit is usually set by the decrease in current; with the valve it is possible to use larger currents because potentials nearer the sparking potential can be applied without danger.

But the advantage to which attention is drawn here is that the thermionic valve can be used on the unstable part

* *Footnote added later.*—A method somewhat similar to this is described in British Patent No. 243349 (Ranger).

† But I have been unable to trace the reference.

of the characteristic, where the currents are greater and yet large separations of the characteristics along the axis of potential are to be found. (An ohmic resistance could be used in this region, but the resistance and the battery voltage required would be so large as to make it almost impracticable.) The relations between light and potential across the cell are somewhat complicated in this region; to understand them we must examine the family of characteristics.

Fig. 2.

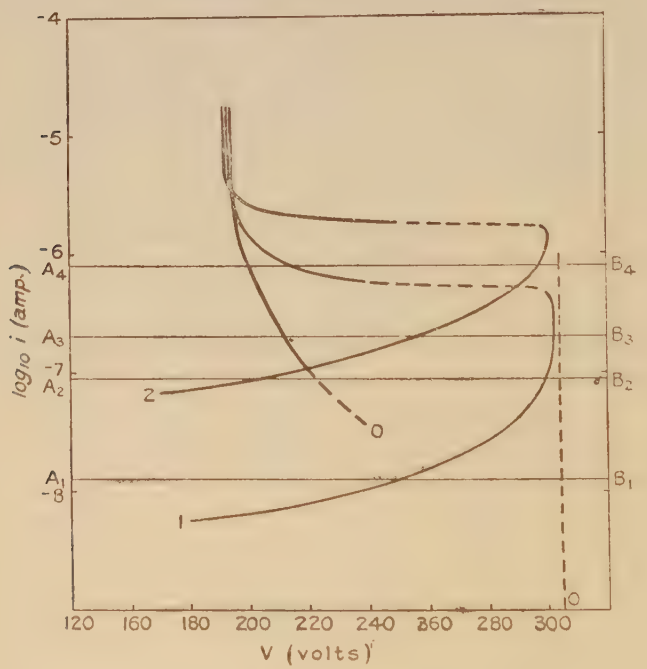


Fig. 2 shows part of the characteristics of a spherical cell for two different illuminations (curves 1 and 2) and for no illumination (curve 0)*; the ordinates are the logarithms of the current, the abscissæ the potential difference across the cell. The larger illumination 2 is about 70 times the smaller 1. The lower part, sloping up to the

* These characteristics refer to a cell different from that of fig. 6 in the previous paper. At first sight they seem very different; but examination will show that, except possibly for no illumination, the difference is one of scale not of form. The part shown is that which corresponds to the part OXPQ.

right, is the stable Townsend discharge, the part of the characteristic which is usually employed. The discharge becomes unstable when the sharp turn to the left occurs and, hereafter, though the discharge is stabilized by the current limiter, it is intermittent. The frequency of intermittence is very small at first, but increases towards the left. Until it becomes about 10 per second, an electrostatic voltmeter across the cell quivers or vibrates and no mean potential can be read; accordingly this part of the curve is dotted. When the frequency increases, the instrument shows a steady value and the continuous curve can be traced. When the cell is illuminated, the form of the curve is independent of the voltage applied to the circuit, so long as it is always greater than the sparking potential; the excess voltage is taken up by the valve, the current through which is saturated. But when there is no illumination, the potential across the cell is practically equal to the applied voltage so long as it is not greater than the sparking potential, whatever the filament current in the valve; if it is greater, the discharge is always intermittent, and the curve cannot be traced until the frequency of intermittence becomes sufficiently high; it then has the form shown by the curve marked O. If any current less than that corresponding to the lower end of this curve is to be used, the applied voltage must be less than the sparking potential; for our purpose this part of the characteristic may be taken to be the vertical dotted line marked O just below the sparking potential.

If the filament current of the valve is set to give a saturated emission represented by one of the lines AB, the potential across the cell for any illumination will be that at the point where the line cuts the corresponding characteristic. In the region A_1B_1 the conditions are similar to those obtained with an ohmic resistance; if changes of illumination from zero are to be measured, the potential applied must be less than the sparking potential; as the illumination is increased, the potential across the cell falls and that across the resistance rises; the change of potential is greater the smaller the current for which the valve is set. For the remaining lines, the applied voltage must be greater than the sparking potential; at A_2B_2 a change from dark to the small illumination 1 produces an increase in the potential across the cell, the larger illumination 2 a decrease. At A_3B_3 the smaller illumination produces an increase, the larger a smaller increase. At both these lines the discharge is stable in the illuminated cell and unstable in the dark cell. At A_4B_4 the small illumination produces a decrease and the

large a larger decrease, and only the large illumination gives stability. The relation between potential and illumination is therefore complicated, if a very large range is considered; but if, as is usual, only a small range of illumination is relevant, the changes are much simpler; the change of potential, whatever its sign, is nearly proportional to the illumination.

This method is most suitable for use with spherical cells: the potential changes in the plane cells are smaller. The exact experimental arrangements will differ with the problem; sometimes it is best to read the potential across the cell, sometimes that across the valve (which is, of course the difference between the applied potential and that across the cell); and when small potential changes are to be investigated, it is often convenient to balance out most of the potential by connecting one of the electrodes of the voltmeter to the insulated electrode and the other to a potentiometer across the battery. But if the principles are understood their application will be obvious. As an example of the results obtainable by the method, the following may be given. An illumination for which the maximum current on the stable part of the characteristic was 10^{-8} amp. gave a change of 15 volts on the unstable characteristic when the current flowing through the cell was 6×10^{-7} amp. To obtain the same change across a high resistance used on the stable portion, this resistance would have to be greater than 1500 megohms. Moreover the greater current has the advantage that all insulation troubles vanish.

The Third Method. Very Small Illuminations.

In the third method, which is suitable for very small illuminations, the change of frequency along the dotted part of the characteristics is used. Since the frequency of the intermittence or oscillation increases from right to left along the unstable portion, and since, of two characteristics corresponding to the very nearly equal illuminations, that for the larger illumination is to the right, if the current is set in the limiter so that AB intersects the dotted portions of both, an increase of illumination will involve a decrease of frequency. This change of frequency can be used as an indication of small illuminations. A telephone is inserted in one of the battery leads, the capacity of the insulated connexion between cell and valve is reduced to a minimum, and the filament current of the valve is varied by a fine adjustment. With the cell in the dark the current is set so

that the frequency of the oscillations, indicated as clicks in the telephone, is about 2 per second; it will not be perfectly regular but a definite value can be obtained by counting for 30 seconds. A very small illumination will then produce a change in the frequency which can be detected by counting the clicks. A further increase will stop the clicks altogether.

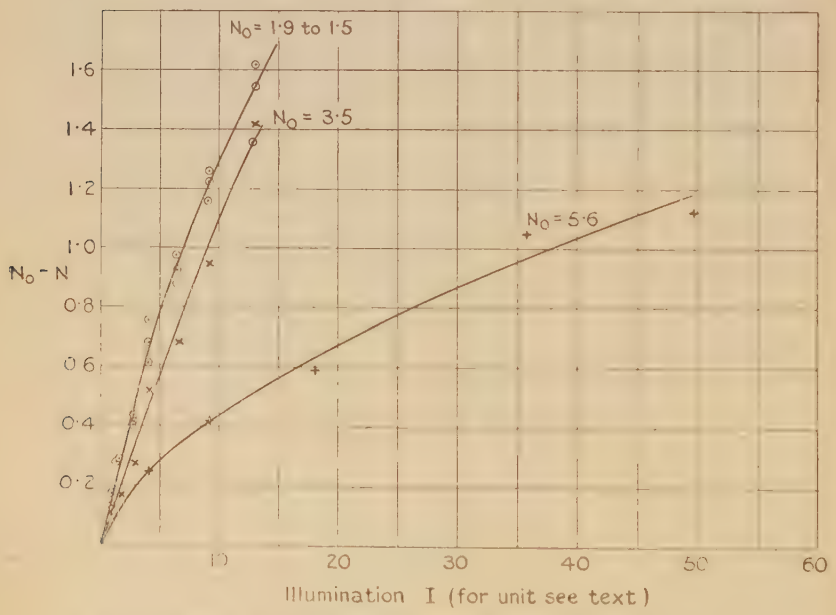
This method is only suitable for use with spherical cells. With the plane cells the changes in the frequency produced by illumination are not completely reversible, probably because the large area of insulated glass surface permits the accumulation of charges. But the sensitivity and convenience of the method are very remarkable. It is possible to detect quite certainly an illumination which would produce in the ordinary manner on the stable part of the characteristic a current of not more than 3×10^{-13} amp.; such an illumination would be given by a source of 1 candle power, at a temperature of 2600° K, at a distance greater than 1 km. Moreover, there is nothing delicate or sensitive about any part of the apparatus. No great constancy of the battery is required; for variations in its potential fall on the valve, not the cell, and produce small changes in the current determined by the failure of complete saturation. Perfect insulation is not necessary; a selected commercial receiving valve can be used *; the connexions can be made by ordinary insulated wire without electrostatic shielding. The readings can be taken from any position to which two pairs of wires can be brought, one to the telephones and the other to the filament rheostat. This rheostat must be well-constructed; but a good quality sliding rheostat used as a shunt across a fixed resistance of much lower value will serve the purpose. And the cell must be suitable; the sensitization of its cathode must have been conducted properly, and the characteristic of the cell must not change greatly when it is exposed to strong light or a glow discharge passed through it; suitable cells can now be purchased from several sources, although there are still some on the market which are quite unsuitable. Insistence on these features may perhaps be pardoned; for scepticism is natural whether the difficulties of measuring photoelectric currents of this magnitude can be avoided so easily. The fact to which the method owes its advantages is

* The current through the insulation of the valve must be small compared with the thermionic current; in commercial valves the conductivity of the insulation in the cap or of the magnesium on the interior glass surface may sometimes be too large. A "bright" emitter is preferable to a "dull" emitter, because the current is more nearly saturated in the former.

that very small currents independent of circumstances over a wide range may be obtained by using saturated thermionic emission in well exhausted vessels. It should be pointed out that, although the apparatus is somewhat similar, the principle involved is entirely different from that of the Geiger counter *. In that instrument a source of radiation produces clicks in a telephone or similar instrument or increases their frequency. Here the radiation stops the clicks or reduces their number.

The relation between the change in frequency and the illumination is regular and sufficiently simple for the method

Fig. 3.

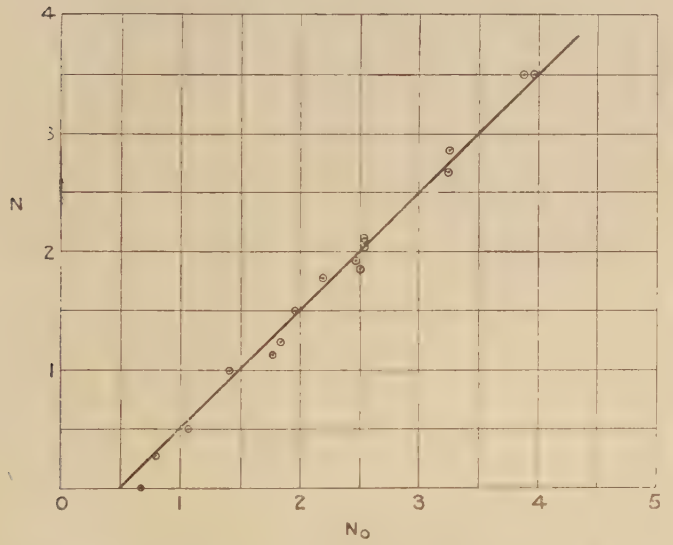


to be used for measurement, with suitable calibration, and not merely for detection. If N_0 is the number of clicks per second in the dark, N the number with illumination I, then over a considerable range $N_0 - N$ is independent of N and approximately proportional to I. The range includes the smallest values of N_0 which it is convenient to count (about 1 a second) and the smallest values of I which can be detected: but when either N_0 or I increases sufficiently, $(N_0 - N)/I$ decreases. These relations are shown in fig. 3,

* *Cf.* e.g. H. Kniepkamp, *Zeit. f. Phys.* xl. p. 12 (1926).

in which $N_0 - N$ is plotted against I; the unit of I is approximately that which would give a maximum current of 5×10^{-13} amp. on the stable part of the characteristic. Each point in the figure gives a value obtained by counting ticks for a single pair of periods each of 30 seconds, one without the illumination and the other with it. After the valve has been running for about $\frac{1}{4}$ hour, N_0 remains constant within 1 per cent. for many minutes; but immediately it is turned on, the variation may be much more rapid. Curve I contains points for which N_0 varied from 1·9 to 1·5; no consistent variation of $N_0 - N$ with N_0 within this range can be detected. The curve they define is very nearly straight in its lower portion, but for higher values of I it falls away. Curves II and III correspond to greater values of N_0: here the values of $N_0 - N$ are smaller and increase much less rapidly with I. Fig. 4, in which N is

Fig. 4.



plotted against N_0 for I = 3, shows how nearly $N_0 - N$ is independent of N_0 when N_0 and I are sufficiently small: the straight line equally inclined to the axes is that on which the points should fall if it were exactly independent.

If an attempt is made to measure by this method illuminations greater than those shown in fig. 3, the difficulty is encountered that, unless N_0 is so great that the ticks can hardly be counted, N is zero. It can be removed by inserting

capacity across the cell, whereby $(N_0-N)/I$ is reduced. But this procedure is not very convenient, because N_0-N varies somewhat rapidly with N_0, even when N_0 is small, unless I is also small. It is usually possible in such cases to reduce I without inconvenience, so as to bring it within the range suitable to the method; but if this should not be practicable, the illumination will be found to be within the range of the second method in its most sensitive form.

The Fourth Method. Technical Applications.

The fourth method also uses a change of frequency to detect the light, but it works in another region where the characteristic changes from unstable to stable. If the curves of fig. 2, or the corresponding curves for a plane cell, are carried further in the direction of greater current, a stage is reached at which the discharge passes into the ordinary stable glow discharge. As the current increases so does the frequency of the oscillation; it passes eventually into the upper part of the audio-frequency range (5000 to 10,000 per second); when the stable part of the characteristic is reached, the oscillations suddenly cease. If the current is adjusted just below that at which the oscillations cease and a moderate illumination is applied to the cell, the oscillations cease, because the current which lies on the unstable portion of the dark characteristic lies on the stable portion of the illuminated characteristic. The characteristics lie so near together in this part that it is almost impossible to separate them by ordinary current and potential measurements; indeed in the previous paper they were said to coincide; but this observation shows that they do not coincide exactly.

The discharge in this region is not exactly reversible. If the current is set so that the smallest possible illumination stops the oscillations, they will not start again when the illumination ceases. This defect is serious in the spherical cells, which are not suited for this method unless large illuminations are to be used. It is much less serious in the plane cells; with them the method is suitable for moderate illuminations, such as that given by a 60-watt gasfilled lamp at the distance of 3 metres.

The method is not likely to be of much use in the laboratory, but it may have technical importance. Thus in the transmission of pictures by radiotelegraphy, the current controlled by the light should be of high audio-frequency.

This form is usually obtained by interposing in the light-beam a rapidly rotating "chopper." By this method the chopper can be dispensed with, and the cell itself made to give oscillations of suitable frequency which are stopped by the light. The only difficulty is that the current must be controlled within 2 or 3 per cent. by regulating the filament current of the valve; but since the mean current is constant and independent of the light, it can be indicated on a direct-current instrument and regulated by hand, or possibly by some automatic relay.

The detection of light by means of change of frequency can be applied to the unstable parts of the characteristic intermediate between the two extremes, where stability passes into instability, which have been considered here in the third and fourth methods. But in these intermediate regions this method will usually be less convenient than the second.

Finally it should be observed that these methods have been worked out with cells not primarily designed for them, but copied from existing models. It is possible that still better results might be obtained if a special type of cell were developed for each method. But on this point we have as yet no information.

CIII. *A Proposed Experiment on Resonance Radiation and a Derivation of the Formula for the Doppler Shift of Scattered or of Resonance Radiation*.* *By* Arthur Edward Ruark, *Ph.D.*

1. WHEN light of wave-length 2536 Å from a mercury resonance lamp is allowed to fall upon a bulb containing mercury vapour heated above 275°, a considerable part of it is regularly reflected †. The same is true for slightly shorter wave-lengths, even though they are incapable of exciting resonance radiation in rarefied mercury vapour. If the vapour density is decreased, the reflexion ceases to be regular. The incident beam penetrates farther and farther into the vapour, as the distance between atoms increases, until finally we have the usual resonance radiation spreading out in all directions from the path of the beam.

* Communicated by the Author. Published by permission of the Director, Bureau of Standards, Department of Commerce.

† Wood and Kimura, Phil. Mag. xxxii. p. 329 (1916). Wood, Phil. Mag. xliv. p. 1105 (1922).

There can be no doubt that when the atoms are sufficiently far apart to act independently, resonance radiation results from absorption followed by emission : it is *not* scattered as soon as it arrives, but there is a finite time during which it is held by the atom. When *and only when* the resonators cease to act independently, phase relations are set up between the contributions of neighbouring atoms. At the highest vapour densities used, there can be no doubt that the regular reflexion is caused by scattering in phase. The question is, what is occurring at intermediate vapour densities? First, we might suppose that the mechanism of each individual act of re-radiation gradually changes; that is, we might postulate the existence of hybrid processes which partake of the characteristics of both resonance and scattering. An alternative view is that the relative number of scattering processes and of absorptions followed by emissions gradually undergoes a change as the mean free path varies.

The indefinite and elastic character of the first suggestion makes it difficult to devise an experiment capable of deciding the question. However, the main purpose of this note is to suggest a series of experiments on these phenomena, which will certainly add to our understanding of the distinction between resonance and scattering. It is very desirable that studies be made on the space distribution of the light sent out by mercury vapour under the conditions described above. These experiments should be carried out at different vapour pressures, and with the incident beam polarized in various ways, as well as unpolarized. Further, the polarization of the emitted light should be studied in the neighbourhood of the regularly reflected beam. So far as I know, this is the only case in which we are able to control and to study accurately the properties of *partially incoherent* light beams, that is, beams in which a portion of the resonators radiate with random phases.

2. It is of interest to obtain formulæ for the frequency of radiation scattered by a moving atom, and for that of resonance radiation from such an atom. One might think these formulæ would be different because the physical processes involved are radically distinct, but we shall show by an easy method that such is not the case.

Schrödinger, using the concept of needle quanta, has derived * a formula for the Doppler shift of the radiation from a moving atom. His formula is not the same as the classical one obtained by applying the Lorentz transformation

* *Phys. Zeit.* xxiii. p. 301 (1922).

to the frequency of a resting harmonic oscillator which emits a spherical wave. If an atom radiates a directed quantum its velocity must change, and as a result both its initial and its final velocity should appear in the expression for the frequency.

Schrödinger's method of attack is as follows:—Let E_1 be the energy which the atom would possess if it were at rest before emission; V_1, its velocity relative to the observer; C, the velocity of light; $\beta_1 = V_1/C$; while θ_1 is the angle between V_1 and the direction of the quantum. Let V_1 have direction cosines l_1, m_1, n_1. The same letters with the subscript 2 denote the corresponding quantities after the quantum $h\nu_2$ has been emitted with direction cosines L_2, M_2, N_2.

Conservation of energy and of the three components of momentum give us the equations:

$$\frac{E_1}{\sqrt{1-\beta_1^2}} = \frac{E_2}{\sqrt{1-\beta_2^2}} + h\nu_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\left.\begin{aligned} \frac{E_1\beta_1 l_1}{\sqrt{1-\beta_1^2}} &= \frac{E_2}{\sqrt{1-\beta_2^2}} + h\nu_2 L_2, \\ \frac{E_1\beta_1 m_1}{\sqrt{1-\beta_1^2}} &= \frac{E_2\beta_2 m_2}{\sqrt{1-\beta_2^2}} + h\nu_2 M_2, \\ \frac{E_1\beta_1 n_1}{\sqrt{1-\beta_1^2}} &= \frac{E_2\beta_2 n_2}{\sqrt{1-\beta_2^2}} + h\nu_2 N_2. \end{aligned}\right\} \quad . \quad . \quad . \quad (2)$$

From these it follows that

$$\nu_2\left(\frac{1-\beta_1\cos\theta_1}{\sqrt{1-\beta_1^2}} \cdot \frac{1-\beta_2\cos\theta_2}{\sqrt{1-\beta_2^2}}\right)^{\frac{1}{2}} = \nu^* \equiv \frac{E_1-E_2}{h} \cdot \frac{E_1+E_2}{2\sqrt{E_1E_2}}. \quad . \quad . \quad . \quad (3)$$

The quantity ν^* is analogous to the frequency of a source at rest in the usual treatment of the Doppler effect, for $\nu=\nu^*$ if $\theta_1=\theta_2=0$ and $v_1=-v_2$.

Dirac has pointed out that Schrödinger's calculations lead to an alternative expression of the result †. It is a consequence of (1) and (2) that

$$E_1\phi_1 = E_2\phi_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$\phi_i = \frac{1-\beta_i\cos\theta_i}{\sqrt{1-\beta_i^2}}; \quad i = 1, 2.$$

† Proc. Cambridge Phil. Soc. xxii. p. 432 (1924).

By equation (4) we can eliminate the factor $\frac{1-\beta_1\cos\theta_1}{\sqrt{1-\beta_1^2}}$ from (3), obtaining

$$\nu_2\frac{1-\beta_2\cos\theta_2}{\sqrt{1-\beta_2^2}}=\nu'\equiv\frac{E_1-E_2}{h}\cdot\frac{E_1+E_2}{2E_2}. \quad . \quad . \quad . \quad (5)$$

Aside from the substitution of ν' for the rest-frequency of an oscillator, this is identical with the usual formula for the Doppler shift.

A slight extension of these results yields us the formula for the Doppler shift in scattered radiation. All quantities characteristic of the incident quantum will be written with the subscript zero, and are to be considered as known, while the subscript 2 indicates quantities belonging to the quantum of scattered radiation.

(1) and (2) are replaced by

$$\frac{E_0}{\sqrt{1-\beta_0^2}}+h\nu_0 \quad =\frac{E_2}{\sqrt{1-\beta_2^2}}+h\nu_2, \quad . \quad . \quad . \quad . \quad (1')$$

$$\frac{E_0\beta_0 l_0}{\sqrt{1-\beta_0^2}}+h\nu_0 L_0=\frac{E_2\beta_2 l_2}{\sqrt{1-\beta_2^2}}+h\nu_2 L_2, \text{ etc. } . \quad . \quad (2')$$

If $E_2=E_0$, we are dealing with ordinary scattering; if $E_2\neq E_0$, the problem is one of scattering accompanied by a change in the quantized energy of the scatterer. For a given direction of scattering these equations, together with $l_2^2+m_2^2+n_2^2=1$, will yield the values of β_2, ν_2, l_2, m_2, and n_2. However, *these will be identical with the values obtained in the case of absorption followed by re-emission after a finite time*; for the absorption is governed by the equations :

$$\frac{E_0}{\sqrt{1-\beta_0^2}}+h\nu_0 \quad =\frac{E_1}{\sqrt{1-\beta_1^2}}, \quad . \quad . \quad . \quad . \quad (1'')$$

$$\frac{E_0\beta_0 l_0}{\sqrt{1-\beta_0^2}}+h\nu_0 L_0=\frac{E_1\beta_1 l_1}{\sqrt{1-\beta_1^2}}, \text{ etc., } . \quad . \quad . \quad (2'')$$

which together with (1), (2) yield us (1'), (2').

This greatly simplifies the problem of the Doppler shift in scattering. By (5) we may write

$$\nu_0\frac{1-\beta_0\cos\theta_0}{\sqrt{1-\beta_0^2}}\cdot\frac{2hE_0}{E_1^2-E_0^2}=\nu_2\frac{1-\beta_2\cos\theta_2}{\sqrt{1-\beta_2^2}}\cdot\frac{2hE_2}{E_1^2-E_2^2}. \quad (6)$$

If the atom is in the same quantized state after scattering as it was before, $E_2=E_0$ and equation (6) becomes

$$\nu_0\frac{1-\beta_0\cos\theta_0}{\sqrt{1-\beta_0^2}}=\nu_2\frac{1-\beta_2\cos\theta_2}{\sqrt{1-\beta_2^2}},$$

which differs from the classical formula since β_2 appears in the right-hand member in place of β_0. This corresponds to the fact that the recoil of the atom introduces a very small frequency change analogous to the Compton shift. In fact, if we neglect the refinements of special relativity and omit terms containing $(\Delta\lambda)^2$, the wave-length shift due to this cause is found to be

$$\Delta\lambda = \frac{2h}{Mc}\sin^2\frac{\phi}{2},$$

where ϕ is the angle of scattering and M the mass of the atom. $\Delta\lambda$ is always less than 3×10^{-5} Ångström unit.

At first sight it appears that ν_2 depends on the energy E_1 which in general does not correspond to a possible quantized state, but it must be remembered that E_1 is only an auxiliary quantity defined by (1″) and (2″). By the use of these equations it may be eliminated.

The method outlined in this paper can be extended to deal with any case of multiple scattering, absorption, or emission, however complicated.

It is illuminating to express the analysis of this section in terms of tensorial relations in a 4-dimensional space-time continuum. This gives a much clearer view of the significance of invariance relations such as (4), (6), and (6′). At the same time it indicates a method of solving the Doppler shift problem in curved space time.

3. Compton * found it convenient to postulate that "if two methods of scattering result in the same relative wave-lengths at different angles, they will also result in the same relative intensity at different angles." If this were true, the experiments on the space distribution of radiation from Hg vapour, suggested in section 1, could not lead to a decision between various views as to the mechanism of re-radiation. It is very probable that this assumption is incorrect. Wave-length shifts depend on the principles of conservation of energy and momentum. Distribution of intensity depends on these principles and also on the orientation of the atom before, after, and perhaps during the scattering process. The equations expressing the conservation of angular momentum will in general be different for various methods of scattering, as can be seen from the problem discussed in section 2. The correspondence principle also speaks in favour of different distributions of intensity

* Phys. Rev. xxi. p. 483 (1923).

over angle. For example, the intensity-distribution from a moving linear oscillator may be altered by changing the orientation of its axis, although the frequency-distribution remains the same.

I wish to thank Dr. Alexander Ellet for very helpful discussion of this paper.

Bureau of Standards,
July 28, 1925.

Note added to proof.—Since this paper was written the advent of the new mechanics makes it possible to calculate the distribution of intensity over angle corresponding to any given mechanism for scattering, so that definite answers can now be given to the questions discussed in section 3.

CIV. *Ionization by Collision.*

By H. G. L. Huxley, *New College, Oxford* *.

1. IN a recent paper "On the Sparking Potentials of Discharge Tubes containing carefully Purified Electrodes," published in the 'Proceedings of the Royal Society' (A. xiv. 1927), J. Taylor has advanced a theory of sparking potentials which calls for some comment.

The usually accepted theory is that of Townsend, which is based upon his theory of ionization by collision in which both electrons and positive ions are assumed to produce new ions by collision with the molecules of the gas in cases where the pressure is large and the sparking potential is above the minimum.

On this hypothesis if a number, n_0, of electrons is liberated from a plane metal cathode and moves through the gas under the action of a uniform electric field, the number, n, arriving at the anode is given by

$$n = n_0 \frac{(\alpha - \beta)\epsilon^{(\alpha-\beta)d}}{\alpha - \beta\epsilon^{(\alpha-\beta)d}}, \quad \ldots\ldots \quad (1)$$

where α is the average number of molecules ionized by an electron in moving through one centimetre of the gas in the direction of the electric force, β the average number ionized by a positive ion, and d the distance in centimetres between the plane parallel electrodes.

* Communicated by Prof. J. S. Townsend, F.R.S.

As d is increased a value S is attained at which

$$\alpha/\beta = \epsilon^{(\alpha-\beta)S},$$

and at this distance a discharge occurs, the sparking potential V being $X \times S$. This theory also explains the critical force at the surface of a wire required to start a corona discharge.

2. In the theory advanced by Taylor a radical change is made, in that, while the same significance is attached to α, the positive ions are assumed no longer to ionize the molecules of the gas but to cause electrons to be set free from the cathode. This is supposed to be accomplished when on neutralization at the cathode the positive ions emit radiation causing the photoelectric emission of electrons from the cathode. Thus when a number n of positive ions arrive at the cathode a certain number γn of electrons are set free, γ being a constant depending on the nature and condition of the electrode. This hypothesis leads directly to the following formula for the current in a gas between plane parallel electrodes :

$$n = n_0 \frac{\epsilon^{\alpha d}}{1-\gamma(\epsilon^{\alpha d}-1)}, \quad \ldots \quad (2)$$

where n and n_0 have their former meanings.

According to this equation the condition for self-maintenance of the current between plane parallel electrodes for a given force X is that the distance between the electrodes should be given by the equation

$$\epsilon^{\alpha S} - 1 = 1/\gamma.$$

Formula (2) is seen to have a form almost identical with Townsend's formula in α and β by writing $\gamma = \beta'/\alpha - \beta'$.

Townsend* has dealt with the case where γ is due not to photoelectric emission at the cathode, but to the direct liberation of electrons by bombardment of the cathode with positive ions, and shows that such a hypothesis is unable to give a satisfactory explanation of currents in gases in the two cases where a discharge is obtained between parallel plates and between coaxial cylinders.

The purpose of this note is to emphasize the fact that on Taylor's hypothesis it is impossible to explain the principal features of the phenomena characteristic of these discharges.

3. In discharges between a wire and a coaxial cylinder it is found that the critical force X, at the surface of the wire

* 'Electricity in Gases,' p. 330.

necessary to initiate the discharge, is independent of the diameter of the outer cylinder provided the latter exceeds a certain value. Experimenters who have studied these phenomena are in general agreement on this point. It indicates that the production of ions in the gas by collisions is confined to a region near the wire. In the case of positive discharges it follows that if the discharge depends on the liberation of electrons from the outer cylinder, the number set free is independent of the diameter of the outer cylinder. Also since the force at the surface of the outer cylinder is diminished when the radius is increased, the quantity γ in Taylor's hypothesis must be independent of the force at the negative electrode.

The sparking potential V for parallel plates is well known to be a function of the product of the pressure p of the gas and the distance S between the plates. The sparking potentials for air, hydrogen, and helium, found by Townsend, are given in the following tables, with the corresponding values of the product $p \times S$, the potentials being in volts, p in millimetres of mercury, and S in centimetres. The sparking potentials were measured with the same apparatus as was used to determine α/p in terms of X/p. The latter quantity is V/pS, and the corresponding values of α/p are given in the third column of the table.

Table I.—Air.

V.	$S \times p$.	X/p.	α/p.	$(\epsilon^{\alpha S} - 1)$.
803	6·12	131	1·30	2880
603	3·45	175	2·13	1550
407	1·15	354	5·2	395
365	·83	440	6·2	170

Table II.—Hydrogen.

V.	$S \times p$.	X/p.	α/p.	$(\epsilon^{\alpha S} - 1)$.
675	12·9	52·5	·41	200
395	4·56	86·6	1·12	164
282	1·62	174·0	2·3	40

For simplicity the gas may be supposed at one millimetre pressure, so that the second column gives the distance between the plates for the sparking potential V and the numbers in the fourth column give α. The values of $(\epsilon^{\alpha S}-1)$ are given in the fifth column.

If these discharges also be dependent on the liberation of electrons from the negative electrode, the numbers in the fifth columns give $1/\gamma$.

Thus the properties of the corona discharge indicate on Taylor's hypothesis that γ is constant, while the properties of discharges between parallel plates show a large variation of γ with the value of X.

Experiments with monatomic gases similar to those mentioned above are being made in the electrical laboratory, but they have not yet been completed. The values of α/p in terms of X/p have been determined by Ayres* for helium, and with a similar apparatus Townsend and McCullum have verified his results and also found the sparking potentials. Examples of these results are given in Table III. In these cases where the sparking potentials are small, it is important to take into consideration the distance that the electrons move from the negative electrode before they acquire sufficient energy to ionize molecules. For this purpose it is sufficient to take $S\left(1-\frac{20}{V}\right)$ instead of S in the expression $(\epsilon^{\alpha S}-1)$ in order to find $1/\gamma$.

Table III.—Helium.

V.	$S\times p$.	X/p.	α/p.	$1/\gamma$.
192	16·0	12·0	·373	215
172	11·2	15·2	·48	116
154	6·4	24·0	·72	55
149	4·8	31·0	·90	42
148	3·2	46·0	1·25	34

In view of these results it is obvious that Taylor's hypothesis cannot give a satisfactory explanation both of the experiments with coaxial cylinders and with parallel plates.

* Phil. Mag., Feb. 1924, p. 410.

It may also be mentioned that if Taylor's hypothesis were adopted, it would be impossible to explain the large difference between the force at the surface of a wire required to start a positive discharge and that required to start a negative discharge.

4. With reference to his hypothesis Taylor states*: "It is readily seen how this hypothesis can be fitted into the relation obtained by Holst and Oosterhuis."

Since one of the fundamental assumptions in the theory of these physicists is that the positive ions produce no ions in collision with the molecules of the gas, the above considerations show that this theory also is open to the same objections as have been indicated above. There is in addition an unreliable assumption in the theory adopted by Holst and Oosterhuis as to the process of the genesis of ions by the collisions of electrons with molecules of the gas, which is based upon one of the theories of ionization proposed by J. Franck and G. Hertz †.

According to this theory, the electrons lose no energy in collisions with the molecules of the gas until they have attained the energy corresponding to the ionizing potential, and having attained that amount of energy they ionize the molecules with which they collide. The evidence in support of this theory is unsatisfactory, as all disagreements between currents indicated by the theory and those obtained experimentally were attributed to impurities.

In applying this theory to their experiments, Holst and Oosterhuis make a correction for small losses of energy proportional to the ratio of the mass of the electron to the mass of the molecule, which may occur in many collisions.

Townsend in a paper, "Ionization by Collision" ‡, shows that in some cases this theory predicts currents which differ by a factor of 10 from those found experimentally.

It is no argument therefore in favour of Taylor's hypothesis to be able to state that it can be fitted into the relation obtained by Holst and Oosterhuis.

5. The question of the emission of electrons from the cathode by the action of positive ions has been studied very carefully by E. Dubois §. In a series of investigations upon the variations in the measurement of sparking potentials, Dubois has shown that these variations are due almost

* *Loc. cit.* p. 82.

† *Phys. Zeit.* xvii. p. 430 (1916).

‡ Phil. Mag. xiv. March 1923, p. 453.

§ "Recherches sur le Potential disruptif dans les gas," *Annales de Phys.* tome xx. (1923).

entirely to the presence of impurities, especially alkaline salts, upon the electrodes. He has investigated methods of eliminating these impurities, and finally concludes that with perfectly clean electrodes the sparking potential is independent of the nature of the metal of which the electrodes are made. Dubois finds that slight traces of salts of the alkali metals, on the surfaces of electrodes, has the effect of improving the conductivity, and he attributes this effect to the action of positive ions in causing electrons to be set free, by bombardment, from impurities on the surface. Dubois' conclusions indicate, therefore, that with ordinary metal electrodes the emission from the cathode is negligible compared with the action of the positive ions in ionizing molecules of the gas, when gases are at pressures above that corresponding to the minimum sparking potential; for it is very improbable that the emission from all these metals is the same.

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CV. *The Thermal Conductivity of Gases.* *By* E. O. Hercus, *M.Sc., and* Prof. T. H. Laby, *M.A., Sc.D.* *

MESSRS. Gregory and Archer † have recently published accounts of new measurements, by the hot-wire method, of the thermal conductivity of gases. They have introduced some important modifications and refinements of the method, but have failed to allow for a source of error, which is considerable at low pressures and with fine wires: namely, the temperature discontinuity between the gas and the hot wire. The existence of this has been shown by Smoluchowski ‡ and confirmed by Knudsen § and later by Langmuir ‖. We have recalculated Gregory and Archer's results, allowing for this effect, using values given by Knudsen. This makes it possible from their first paper ¶ to

* Communicated by the Authors.

† Proc. Roy. Soc. A, cx. p. 91 (1926); Phil. Mag. (7) i. p. 593 (1926).

‡ *Wied. Ann.* p. 101 (1898); see also Soddy & Berry, Proc. Roy. Soc. lxxxiii. p. 254 (1910).

§ *Ann. der Phys.* xxxiv. p. 593 (1911).

‖ Phys. Rev. viii. p. 149 (1916).

¶ Proc. Roy. Soc. A, cx. p. 91 (1926).

deduce the thermal conductivities by a simple and sound method, whereas the method they use is unsound in principle. The experiments described in their second paper * lead to a much better verification of Maxwell's law than they claim, when the allowance is made.

Smoluchowski shows that the temperature drop at the wire is †

$$\gamma \frac{d\theta}{dr},$$

whence it can be shown that values of k calculated in the usual way are subject to a correcting factor:

$$1 + \frac{\gamma}{r_1 \log_e \frac{r_2}{r_1}}.$$

The value of the coefficient γ is related by Knudsen to an accommodation factor a and the mean free path λ thus :

$$\gamma = 1{\cdot}9 \frac{2-a}{2a} \lambda.$$

Gregory and Archer state that the platinum they used was "bright," while Knudsen gives for bright platinum $a = {\cdot}835$ for air, $a = {\cdot}358$ for hydrogen. These values have been used in recalculating the curves shown in the figure.

In their main research on the conductivity of air and hydrogen they use two tubes, wide and narrow. As the pressure is lowered, convection becomes negligible for the narrow tube sooner than for the wide one. If k is to be determined, this must occur in either case before Maxwell's law begins to break down—that is, the heatflow-pressure curve must have a portion parallel to the pressure axis. In discussing their method ‡ they show curves which do not satisfy this requirement, and their argument, though elaborate, does not show any advantage gained by the double set of tubes. When convection is absent, the conductivity k is calculable from a formula :

$$k = \frac{C^2 \frac{R}{l} \cdot \log_e \frac{r_2}{r_1}}{2\pi J \theta}.$$

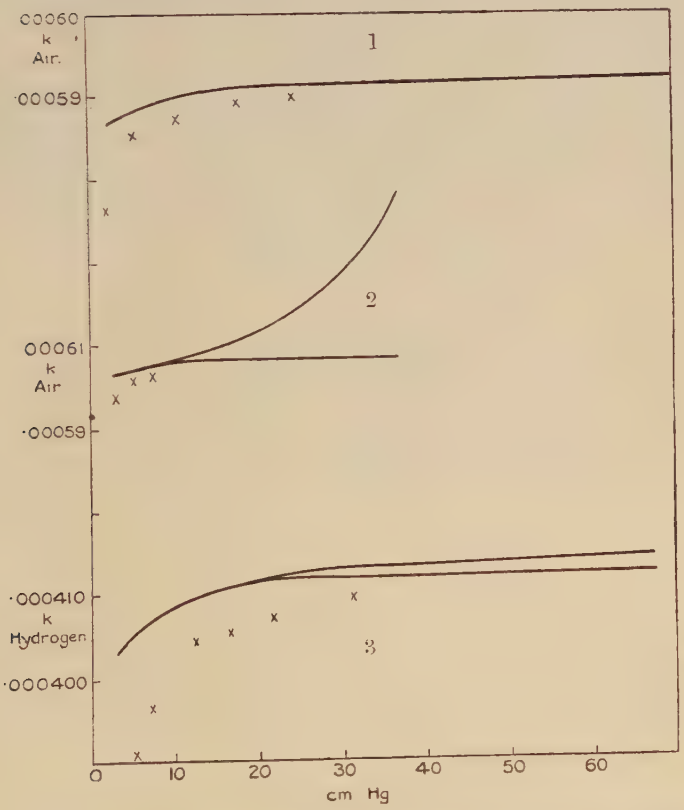
* Phil. Mag. (7) i. p. 593 (1926).

† The gradient $\frac{d\theta}{dr}$ reaches 760 deg. cm.$^{-1}$ in some of Gregory and Archer's work; hence arises a large correction. Yet they criticise the gradient in experiments by us of 32·5 deg. cm.$^{-1}$ as large !

‡ Proc. Roy. Soc. A, cx. p. 100 (1926).

They call the value of this expression the "equivalent conductivity," and plot it, and also C^2, against pressure for the two sets of tubes. Using subscripts to distinguish the narrow and wide tubes,

$$k_N = \frac{C_N^2 \frac{R}{l} \log_e \frac{r_2}{r_1}}{2\pi J\theta}, \qquad k_W = \frac{C_W^2 \frac{R}{l} \log_e \frac{r_3}{r_1}}{2\pi J\theta}.$$



Recalculation of Gregory and Archer's results, allowing for discontinuity of temperature at the surface of the wire, from their observations:

(1) On the validity of Maxwell's law;
(2) On k for air, using wide and narrow tubes;
(3) On k for hydrogen, using wide and narrow tubes.

Original values as computed by Gregory and Archer are shown by crosses (×) where they differ *appreciably* from these new calculated values.

The graphical construction they used amounts to finding, from all the pairs of points for which $k_N = k_W$, the "one pair" for which

$$\frac{C_N^2}{C_W^2} = \frac{\log \frac{r_3}{r_1}}{\log \frac{r_2}{r_1}}.$$

But while they state that one value only satisfies this condition, it is clear that it is a necessary consequence, algebraically, of

$$k_N = k_W;$$

that is, they fail to provide a new criterion for the elimination of convection.

We find from our recalculations of their results, allowing for the temperature discontinuity at the surface of the wire :—

Thermal Conductivities.

Air.		Hydrogen.	
12·062° C.	·0000605	4·218° C.....	·000412
9·749	·0000602	3·298	·000410
7·437	·0000598	2·355	·000409

These values, using temperature coefficients of ·00298, ·00277 for air and hydrogen respectively, give for the thermal conductivities at 0° C.:—

Air.....	·0000585
Hydrogen	·000406

A careful discussion * of the previous determinations of k for air gave as the weighted mean of nineteen observations the value $k_0 = 5{\cdot}35 \times 10^{-5}$, and the weighted mean of twelve observations for hydrogen, $k_0 = 37{\cdot}9 \times 10^{-5}$. Gregory and Archer's and this value differ by a surprisingly large amount, which needs explanation.

* T. H. Laby and Miss E. A. Nelson, International Critical Tables.

CVI. *The Bending of Columns of Varying Cross-section.*—II. *By* J. A. Wilcken, *B.Sc., Ph.D., Lecturer in Electrical Engineering at Armstrong College, Newcastle-upon-Tyne* *.

IN a previous paper † an axially loaded column has been considered, of a varying cross-section specified by (i.) $P/EI=(\alpha+\beta x)^{-4}$, or by (ii.) $P/EI=(\alpha+\beta x)^{-2}$, corresponding to a "straight-tapering" or a "bulging" solid column, respectively, and the extension to steel-frame towers has been indicated. In practice, however, it is usually not safe to assume the load axial, and in the case of a bridge-support or similar structure, the condition is certainly not fulfilled. In modern transmission-line practice, the symmetrical arrangement of conductors is frequently sacrificed, for several reasons, and even though the normal conductor-load may be axial, the snapping of one conductor would submit the mast to an eccentric, though diminished, load, which might become dangerous.

Eccentric Load.

(A)—*A column simply supported at both ends.* Assuming a vertical load P acting at a distance f from the axis, the equation to the bending moment becomes

$$EI\frac{d^2y}{dx^2}+P(y-f)=0 \quad . \quad . \quad . \quad . \quad (40)$$

with the boundary conditions

$$y|^0=y|^l=0. \quad . \quad . \quad . \quad . \quad . \quad (41)$$

(i.) $P/EI=(\alpha+\beta x)^{-4}$. The solution may be written

$$y=f+(\alpha+\beta x)(A\cos\chi+B\sin\chi). \quad . \quad . \quad (42)$$

We use the notation, as previously defined,

$$\left.\begin{aligned}\chi&=(\alpha\beta+\beta^2x)^{-1},\\ \chi_0&=(\alpha\beta)^{-1},\\ \chi_1&=(\alpha\beta+\beta^2l)^{-1},\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (43)$$

* Communicated by the Author.
† Phil. Mag. vol. iii. p. 418 (Feb. 1927).

and get, in place of (41),

$$A\cos\chi_0 + B\sin\chi_0 = -f/\alpha,$$
$$A\cos\chi_1 + B\sin\chi_1 = -f/(\alpha+\beta l),$$

and, substituting in (42) the values of A and B as determined from these equations, we find, after reduction,

$$y = f\left\{1-(\alpha+\beta x)\operatorname{cosec}(\chi_0-\chi_1) \times\left[\frac{\sin(\chi_0-\chi)}{\alpha+\beta l}+\frac{\sin(\chi-\chi_1)}{\alpha}\right]\right\}.$$

Introducing the taper-ratio,

$$\rho_1 = (\alpha+\beta l)/\alpha,$$

and writing

$$\left.\begin{aligned}(\alpha+\beta x)/\alpha &= 1-(1-\rho_1)x/l = \xi_1,\\ \chi_0-\chi_1 &= l/\alpha(\alpha+\beta l) = \lambda_1,\\ \chi_0-\chi &= x/\alpha(\alpha+\beta x) = (\rho_1/\xi_1)(x/l)\lambda_1 = r_1\lambda_1,\\ \chi-\chi_1 &= (1-r_1)\lambda_1,\end{aligned}\right\} \quad (44)$$

we obtain for the deflexion

$$y = f\left\{1-\xi_1\left(\cos r_1\lambda_1 + \frac{1/\rho_1-\cos\lambda_1}{\sin\lambda_1}\sin r_1\lambda_1\right)\right\}. \quad (45)$$

(ii.) $P/EI=(\alpha+\beta x)^{-2}$. The solution is now written

$$y = f+(\alpha+\beta x)^{1/2}(A\cos\chi+B\sin\chi) \quad . \quad . \quad (46)$$

with

$$\chi = \mu\log(\alpha+\beta x),$$
$$\mu = \sqrt{\beta^{-2}-1/4},$$

and assuming μ real. Determining the integration constants A and B from the boundary conditions and substituting in (46), we get

$$y = f\left\{1-(\alpha+\beta x)^{1/2}\operatorname{cosec}(\chi_0-\chi_1) \times\left[\frac{\sin(\chi_0-\chi)}{(\alpha+\beta l)^{1/2}}+\frac{\sin(\chi-\chi_1)}{\alpha^{1/2}}\right]\right\},$$

and, with the notation,

$$\left.\begin{aligned} \rho_2 &= (\alpha+\beta l)/\alpha, \\ \chi_0-\chi_1 &= -\mu \log \rho_2 = \lambda_2, \\ (\alpha+\beta x)/\alpha &= \xi_2, \\ \chi_0-\chi &= -\mu \log \xi_2 = r_2\lambda_2, \\ \chi-\chi_1 &= (1-r_2)\lambda_2, \end{aligned}\right\} \quad . \quad . \quad . \quad (47)$$

we find the deflexion

$$y = f\left\{1-\sqrt{\xi_2}\left(\cos r_2\lambda_2 + \frac{\sqrt{1/\rho_2}-\cos\lambda_2}{\sin\lambda_2}\sin r_2\lambda_2\right)\right\}. \quad (48)$$

Comparing the expressions (45) and (48) with the deflexion of a uniform column,

$$y = f\left\{1-\left[\cos x\sqrt{P/EI} + \frac{1-\cos l\sqrt{P/EI}}{\sin l\sqrt{P/EI}}\sin x\sqrt{P/EI}\right]\right\}, \quad (49)$$

it is seen, that for $\rho_1 = 1$, we have also

$$\xi_1 = 1, \qquad r_1\lambda_1 = (x/l)\lambda_1 = x\sqrt{P/EI},$$

and so the expressions (49) and (45) become identical. Also, when ρ_2 is nearly equal to unity, we write $\rho_2 = 1+\eta$, and so

$$r_2 = \log \xi_2/\log \rho_2 = x/l \quad \text{nearly};$$

and $\beta = (\rho_2-1)\alpha/l = \eta\alpha/l, \quad \mu$ nearly $= 1/\beta = l/\eta\alpha$;

thus $$\lambda_2 = l/\alpha = l\sqrt{P/EI},$$

and (48) becomes identical with (49), for $\eta \to 0$.

The deflexion of a uniform column is thus a special case of either of the two types discussed. The bending moment at any point x becomes:

for a uniform column,

$$Pf\left\{\cos x\sqrt{P/EI} + \frac{1-\cos l\sqrt{P/EI}}{\sin l\sqrt{P/EI}}\sin x\sqrt{P/EI}\right\}; \quad (50)$$

for a column of type (i.),

$$Pf\xi_1\left\{\cos r_1\lambda_1+\frac{1/\rho_1-\cos\lambda_1}{\sin\lambda_1}\sin r_1\lambda_1\right\};\quad .\quad .\quad .\quad .\quad (51)$$

for a column of type (ii.),

$$Pf\sqrt{\xi_2}\left\{\cos r_2\lambda_2+\frac{\sqrt{1/\rho_2}-\cos\lambda_2}{\sin\lambda_2}\sin r_2\lambda_2\right\}.\quad .\quad .\quad (52)$$

It is seen from these expressions, that when the load acts at a finite distance from the axis of the column, there is always a definite deflexion, a definite bending moment, which in every case becomes infinitely large when $\lambda=\pi$, that is, according to (7) and (10) *, when the load becomes equal to the crippling load for a corresponding axially loaded column. Usually, however, the permissible magnitude of bending moment — and our fundamental assumption of a "small deflexion"—will be transgressed long before the load approaches such values, *except when f is very small.*

For a vanishing eccentricity, therefore, the crippling load becomes the limit of permissible loads.

In other cases it is imperative to verify that the maximum bending moment does not exceed the safe value ; and this is comparatively simple for the uniform column, where the maximum occurs at mid-length, and has the value $Pf\sec(\lambda/2)$, λ being $=l\sqrt{P/EI}$. But in a non-uniform column of type (i.), the position of the maximum bending moment depends on the value of the load, and differentiation of the expression (51) leads, on equating the result to zero, to a transcendental equation of a complicated nature, not amenable to simple graphical treatment. A more detailed study of this case will be given later.

Plotting the bending moments, for any given load, for a few points between $x/l=0{\cdot}5$ and $0{\cdot}9$ will usually reveal the position of maximum with sufficient precision.

For a column of type (ii.), we get, on differentiation of the expression (52) and equating to zero,

$$\tfrac{1}{2}\xi_2^{-1/2}\{\cos r_2\lambda_2+u\sin r_2\lambda_2\}\frac{d\xi_2}{dx}$$
$$+\xi_2^{1/2}\lambda_2\{-\sin r_2\lambda_2+u\cos r_2\lambda_2\}\frac{dr_2}{dx}=0,\quad (53)$$

* *Loc. cit.*

writing $u = (\sqrt{1/\rho_2} - \cos\lambda_2)/\sin\lambda_2$; and since

$$r_2 = \log\xi_2/\log\rho_2$$

and so, $$\frac{dr_2}{dx} = (\xi_2 \log\rho_2)^{-1}\frac{d\xi_2}{dx},$$

we have, in place of (53),

$\frac{1}{2}(\cos r_2\lambda_2 + u\sin r_2\lambda_2) + (\lambda_2\log\rho_2)(-\sin r_2\lambda_2 + u\cos r_2\lambda_2) = 0$

leading to

$$\tan r_2\lambda_2 = (2u\lambda_2 + \log\rho_2)/(2\lambda_2 - u\log\rho_2). \quad . \quad (54)$$

This equation gives r_2, and hence ξ_2 and x/l, for any given load and column, and writing

$$\gamma = (2u\lambda_2 + \log\rho_2)/(2\lambda_2 - u\log\rho_2)$$

the maximum bending moment becomes

$$Pf\xi_2^{1\cdot2}(1+u\gamma)(1+\gamma^2)^{-1\cdot2}.$$

Making $\rho_2 = 1$, $\xi_2 = 1$, $u = \tan(\lambda/2)$, the formula for the uniform column is obtained.

If the load on a column of type (ii.) is so small, that μ becomes imaginary, the circular functions are replaced by the corresponding hyperbolic functions, and $\nu = \sqrt{1/4 - \beta^{-2}}$ is substituted for μ. (Cfr. above, *l. c.* p. 423.)

(B)—*A column built in at one end, free at the other end.* For a deflexion h at the free end, the equation is

$$EI\frac{d^2y}{dx^2} + P(y - f - h) = 0, \quad . \quad . \quad . \quad (55)$$

with the conditions

$$y\Big|^0 = 0 = \frac{dy}{dx}\Big|^0, \quad y|^l = h. \quad . \quad . \quad . \quad (56)$$

(i.) $P/EI = (\alpha+\beta x)^{-4}$. The solution is, in our usual notation,

$$y = f + h + (\alpha+\beta x)(A\cos\chi + B\sin\chi),$$

and the boundary conditions become

$$\left.\begin{aligned} A\cos\chi_0 + B\sin\chi_0 + (f+h)/\alpha &= 0, \\ A\cos\chi_1 + B\sin\chi_1 + f/(\alpha+\beta l) &= 0, \\ A\left(\beta\cos\chi_0 + \frac{1}{\alpha}\sin\chi_0\right) + B\left(\beta\sin\chi_0 - \frac{1}{\alpha}\cos\chi_0\right) &= 0. \end{aligned}\right\} \quad (57)$$

To satisfy these equations we must have

$$\begin{vmatrix} \cos\chi_0 & \sin\chi_0 & (f+h)/\alpha \\ \cos\chi_1 & \sin\chi_1 & f/(\alpha+\beta l) \\ \beta\cos\chi_0+\frac{1}{\alpha}\sin\chi_0 & \beta\sin\chi_0-\frac{1}{\alpha}\cos\lambda_0 & 0 \end{vmatrix} = 0,$$

or, after reduction,

$$\cos(\chi_0-\chi_1)-\alpha\beta\sin(\chi_0-\chi_1) = \{f/(f+h)\}\{\alpha/(\alpha+\beta l)\}.$$

Using the taper-ratio and equations (44), this may be written

$$\cos\lambda_1+\frac{1/\rho_1-1}{\lambda_1}\sin\lambda_1 = f/(f+h)\rho_1. \quad . \quad . \quad (58)$$

Evaluating the integration constants A and B from (57) and substituting in the solution above, we find the deflexion

$$y = f+h-(\alpha+\beta x)\operatorname{cosec}\lambda_1\left\{\frac{f+h}{\alpha}\sin(\chi-\chi_1) + \frac{f}{\alpha+\beta l}\sin(\chi_0-\chi)\right\}$$

$$= (f+h)\left\{1-\xi_1\left(\cos r_1\lambda_1+\frac{1/\rho_1-1}{\lambda_1}\sin r_1\lambda_1\right)\right\}. \quad . \quad (59)$$

When $\lambda_1\cot\lambda_1 = 1-1/\rho_1$, corresponding to the crippling load for an axially loaded column, according to equation (30) above (*l. c.*), the deflexion h becomes infinite, since the left-hand side of equation (58) vanishes, and so the crippling load appears once more as a limit, which, however, cannot be safely approached unless also $f=0$.

(ii.) $P/EI=(\alpha+\beta x)^{-2}$. The integration constants A and B in the solution

$$y = f+h+(\alpha+\beta x)^{1/2}(A\cos\chi+B\sin\chi)$$

must now satisfy the conditions

$$\left.\begin{aligned} A\cos\chi_0+B\sin\chi_0+(f+h)/\sqrt{\alpha} &= 0, \\ A\cos\chi_1+B\sin\chi_1+f/\sqrt{\alpha+\beta l} &= 0, \\ A(\cos\chi_0-2\mu\sin\chi_0)+B(\sin\chi_0+2\mu\cos\chi_0) &= 0, \end{aligned}\right\} \quad (60)$$

the consistency of which requires the vanishing of the determinant

$$\begin{vmatrix} \cos\chi_0 & \sin\chi_0 & (f+h)/\sqrt{\alpha} \\ \cos\chi_1 & \sin\chi_1 & f/\sqrt{\alpha+\beta l} \\ \cos\chi_0 - 2\mu\sin\chi_0 & \sin\chi_0 + 2\mu\cos\chi_0 & 0 \end{vmatrix}$$

leading to

$$\cos\lambda_2 + \frac{1}{2\mu}\sin\lambda_2 = f/(f+h)\sqrt{\rho_2}. \quad . \quad . \quad (61)$$

Substituting the values of A and B, as found from the equations (60), in the expression for the deflexion, we find

$$y = f+h-(\alpha+\beta x)^{1/2}\operatorname{cosec}\lambda_2\left\{\frac{f+h}{\sqrt{\alpha}}\sin(\chi-\chi_1) + \frac{f}{\sqrt{\alpha+\beta l}}\sin(\chi_0-\chi)\right\}$$

$$= (f+h)\left\{1-\xi_2^{1/2}\left(\cos r_2\lambda_2 + \frac{1}{2\mu}\sin r_2\lambda_2\right)\right\}. \quad . \quad . \quad (62)$$

According to equations (61) and above, the load corresponding to the crippling load for an axially loaded column would also in this case give an infinitely large deflexion.

The bending moment becomes:

for type (i.), $\quad \mathrm{P}(f+h)\xi_1\left(\cos r_1\lambda_1 + \frac{1/\rho_1-1}{\lambda_1}\sin r_1\lambda_1\right);$

for type (ii.), $\quad \mathrm{P}(f+h)\xi_2^{1/2}\left(\cos r_2\lambda_2 + \frac{1}{2\mu}\sin r_2\lambda_2\right),$

with the usual substitution of hyperbolic for circular functions in case of small loads.

The maximum deflexion h can be obtained from the equations (58) and (61) respectively; the largest bending moment occurs at the foot, $x=0$.

A case of practical importance is where the column is built in at one end ($x=0$) and the other end is free to rotate but cannot deflect, as when a mast is guyed at the top. The results are obtained from the above making $h=0$.

When $f=0$, the load is axial and the general formulæ (59) and (62) become identical with those found previously, (32) and (37).

We may now summarize our results in the following statements :—

For a column of the types discussed, of which the uniform column appears as a special case throughout, simply supported at both ends, the load acting vertically at a distance f from the axis, the bending moment at any point x is given by

$$\mathrm{P}f\xi_1\left(\cos r_1\lambda_1 + \frac{1/\rho_1 - \cos\lambda_1}{\sin\lambda_1}\sin r_1\lambda_1\right) \qquad \text{for type (i.),}$$

$$\mathrm{P}f\xi_2^{1/2}\left(\cos r_2\lambda_2 + \frac{\sqrt{1/\rho_2} - \cos\lambda_2}{\sin\lambda_2}\sin r_2\lambda_2\right) \qquad \text{for type (ii.).}$$

As f decreases towards zero, approaching axial loading, the bending moment will remain finite for loads such as make λ approach π, a condition providing a limiting value for the safe load, if acting axially.

If the column is built in at one end, and free at the other end, the bending moment becomes

$$\mathrm{P}(f+h)\xi_1\left(\cos r_1\lambda_1 + \frac{1/\rho_1 - 1}{\lambda_1}\sin r_1\lambda_1\right) \qquad \text{for type (i.),}$$

$$\mathrm{P}(f+h)\xi_2^{1/2}\left(\cos r_2\lambda_2 + \frac{1}{2\mu}\sin r_2\lambda_2\right) \qquad \text{for type (ii.)}$$

and the deflexion h is determined by the equations

$$\cos\lambda_1 + \frac{1/\rho_1 - 1}{\lambda_1}\sin\lambda_1 = f/(f+h)\rho_1,$$

$$\cos\lambda_2 + \frac{1}{2\mu}\sin\lambda_2 = f/(f+h)\sqrt{\rho_2},$$

respectively. As f approaches zero, these two equations become

$$\lambda_1\cot\lambda_1 = 1 - 1/\rho_1,$$

$$\lambda_2\cot\lambda_2 = \tfrac{1}{2}\log\rho_2,$$

and furnish a limiting value for the load, when axial.

The coefficients ξ and r depend on the position, x/l, and the taper-ratio, $\rho = 1 + \beta l/\alpha$; λ depends in each case on the "crippling load," in the Eulerian sense, and on the actual value of the load P, and may be written $\pi\sqrt{\mathrm{P}/\mathrm{P_E}}$, where $\mathrm{P_E}$ is the crippling load for the corresponding simply supported column, axially loaded.

CVII. *The Jet-Wave Accelerometer attached to a Pendulum.* *By* Jul. Hartmann, *Dr. tech. Docent in the Royal Technical College, Copenhagen* *.

Introduction.

In 1923 Professor K. Prytz published a paper: "L'accélération mesurée au moyen d'une flamme" †. It occurred to me that the flame used by Prof. Prytz may be considered as a jet, and that, consequently, a liquid-jet may be utilized for the same purpose as the flame. During the last year the application of the jet as an accelerometer was discussed and experimentally studied in connexion with a pendulum to which the jet was attached. It is the results of these experiments which is given in the following. A brief account of the general theory of the relative motion of a jet following a moving body has already been given by me in the issue June 6, 1925, of 'Nature.' The publication was caused by a contribution by Mr. Paul Kirkpatrick, who, in No. 2893, April 11, 1925, of the same periodical, had suggested the use of the jet as a means for studying the motion of a body and especially as a means for Seismometry. I have used the name written above the present paper for the accelerometer studied by me because the apparatus is closely related to a series of systems which are all based on a single principle, that of the jet-wave. (The jet-wave oscillograph, the jet-wave rectifier, etc.) As an introduction to the main subject of the paper a brief survey of the general theory of the accelerometer may prove valuable.

Theory of the Jet-wave Accelerometer.

A nozzle is moving on perpendicularly to the axis of the jet or jet-hole. The movement is represented by

$$Y = f(t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the velocity thus being $f'(t)$ and the acceleration $f''(t)$.

As seen from fig. 1, the relative deflexion of a jet-particle

* Communicated by the Author.

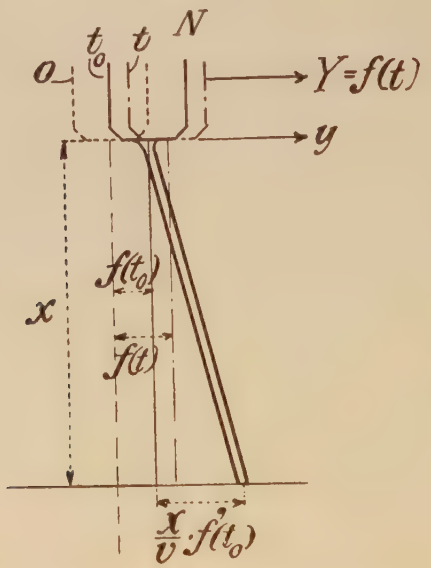
† *Le Journal de Physique et le Radium*, ser. vi. t. iv. (1923).

at a distance x from the nozzle is given by:

$$y = \frac{x}{v} f'(t_0) - [f(t) - f(t_0)]$$
$$= f'(t_0)(t - t_0) - [f(t) - f(t_0)], \quad . \quad . \quad . \quad (2)$$

v denoting the velocity of the jet and $t - t_0$ the time which it takes for a particle of the jet to travel from the nozzle out

Fig. 1.



to a point at the distance x. In replacing $f(t)$ by the series:

$$f(t) = f(t_0) + (t - t_0) f'(t_0)$$
$$+ \tfrac{1}{2}(t - t_0)^2 f''(t_0) + \tfrac{1}{6}(t - t_0)^3 f'''(t_0) \ldots, \quad (3)$$

we get

$$y = -\tfrac{1}{2}(t - t_0)^2 f''(t_0) - \tfrac{1}{6}(t - t_0)^3 f'''(t_0) + \ldots, \quad . \quad (4)$$

or

$$y = \frac{1}{2}\left(\frac{x}{v}\right)^2 f''(t_0) - \frac{1}{6}\left(\frac{x}{v}\right)^3 f'''(t_0) + \ldots . \quad . \quad . \quad . \quad (5)$$

If x is so small that the second term and all the following may be neglected, (5) takes the form:

$$y = -\frac{1}{2}\left(\frac{x}{v}\right)^2 f''(t_0) = -\frac{1}{2}\left(\frac{x}{v}\right)^2 f''\left(t - \frac{x}{v}\right), \quad . \quad (6)$$

i. e. the movement of the hitting point of the jet in a plane perpendicular to the original direction of the jet represents—with a certain delay—the acceleration in the movement of the nozzle. The delay is equal to the time which is taken by the jet in travelling from the jet-hole to said plane.

Exactly the same expression is, of course, derived by applying the relative acceleration—$f''(t_0)$—to the jet-particle and by developing $f'(t)$ in series. We then get

$$\frac{d^2y}{dt^2} = -f''(t) = -f''(t_0) - f'''(t_0)(t-t_0) \ldots, \quad . \quad (7)$$

from which (4) is directly derived when it is remembered that $y=0$ and $\frac{dy}{dt}=0$ at the time $t=t_0$. In this way the accelerometer plainly shows itself as a means for recording mechanical forces, or qualities creating such forces; for instance, electric currents, as in the case of the jet-wave oscillograph alluded to above.

Particularly if

$$Y = Y_0 \sin \omega t = Y_0 \sin \frac{2\pi}{T} t, \quad . \quad . \quad . \quad . \quad (8)$$

we get

$$y = \frac{1}{2}\left(\frac{2\pi x}{\lambda}\right)^2 Y_0 \sin \omega t_0 + \frac{1}{6}\left(\frac{2\pi x}{\lambda}\right)^3 Y_0 \cos \omega t_0 - \frac{1}{24}\left(\frac{2\pi x}{\lambda}\right)^4 Y_0 \sin \omega t_0 \ldots, \quad (9)$$

where $\lambda = vT$. At the instant $t_0=0$ the acceleration is zero, and so is the first term of (9). But the second term assumes the value $\frac{1}{6}\left(\frac{2\pi x}{\lambda}\right)^3 Y_0$, and represents in the main the error committed in measuring the acceleration by the deflexion. At the instant $t_0 = \frac{T}{4}$ the error in the measurement of the acceleration by y is given by $-\frac{1}{24} \cdot \left(\frac{2\pi x}{\lambda}\right)^4 Y_0$.

The Design of the Jet-wave Accelerometer.

We may use the expression (9) as a basis for the design of jet-wave accelerometers. With a view to orientation we will first consider an accelerometer consisting of a jet with a velocity 1000 cm./sec., thus a relatively swift jet. We demand from the accelerometer that the second term of the

expression (9) for y at the time $t_0=0$ shall be a small fraction $\frac{r}{100}$ of the first term at the time $t_0=\frac{T}{4}$. This means, very nearly, that

$$x \leq \frac{r}{100} \cdot \frac{\lambda}{2}. \quad \ldots \ldots \quad (1)$$

If $T=\frac{1}{50}$ sec., then $\frac{\lambda}{2}=10$ cm. Thus, if $r=5$, x must be less or equal to 0·5 cm. With a jet of this length, $y=0{\cdot}1$ cm. will constitute a suitable amplitude. The corresponding value of the amplitude Y_0 of the oscillating body is determined from

$$y=\frac{1}{2}\left(\frac{2\pi x}{\lambda}\right)^2 \cdot Y_0, \quad \ldots \ldots \quad (2)$$

which gives $y_0=8{\cdot}1$ cm. To this amplitude corresponds a maximum acceleration $Y_0\omega^2=800000$, thus more than 800 times that of gravity. An accelerometer such as that indicated will in its outstanding features exactly coincide with a jet-wave oscillograph for tracing pictures of technical alternating currents. The jet should, according to the experiences gained in the development of the oscillograph, be made rather thin, say 0·1 mm. As a contrast we may hereafter consider an accelerometer with a jet of a velocity 50 cm./sec. We assume T to be 5 sec., and find $\lambda/2=125$ cm., from which, if $r=5$, we get $x \leq 6{\cdot}25$ cm. ~ 6 cm. A convenient amplitude in the relative motion will be 1·2 cm. The corresponding value of Y_0 is 105·5 cm., and that of the maximum acceleration $\omega^2 Y_0$ 166·5, *i. e.* about 6 times less than that of gravity. An accelerometer mainly of this type was used in the following research.

The Theory of the Jet-wave Accelerometer attached to a Pendulum.

In order to put the jet-wave accelerometer to test, it was attached to a pendulum, the jet being adjusted in the axis of the pendulum-bar when the latter was in its equilibrium position. In the calculation of the relative motion of a jet-particle all the relative forces or accelerations must be taken into account; namely, apart from the gravity: (1) the radial acceleration $a\omega^2$, ω indicating the angular velocity of the pendulum and a the distance from the axis of revolution of the pendulum to the particle in question; (2) the

tangential acceleration $a\frac{d\omega}{dt}$; and (3) Corioli's acceleration $2\omega v$, v denoting the relative velocity of the particle. Figs. 2 *a* and 2 *b* indicate these forces at two moments during the motion of the pendulum, away from and towards

Fig. 2 *a*.

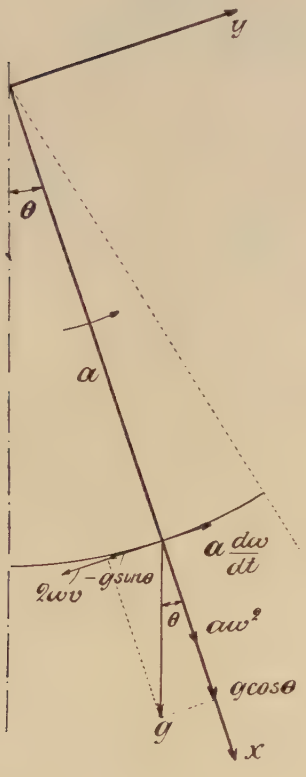
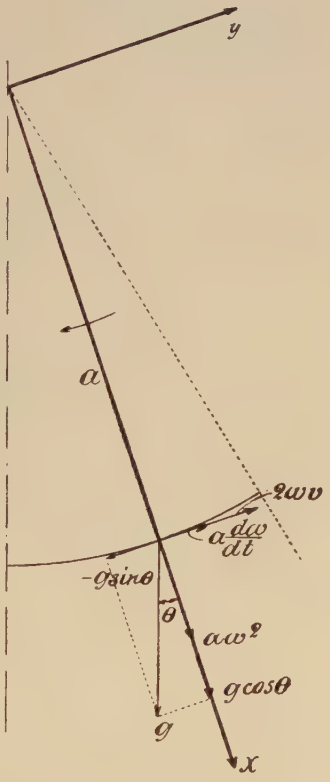


Fig. 2 *b*.



the position of equilibrium. We confine ourselves to considering the relative deflexion of the jet-particle resp. of the jet at so short a distance x from the nozzle that θ, ω, and $\frac{d\omega}{dt}$ may be regarded as approximately constant during the motion of the particle through x. Furthermore, we will assume that the relative deflexion of the jet is always

very small. Then the equations of the relative motion of a particle may be written :

$$\frac{d^2x}{dt^2} = g\cos\theta + a\omega^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{d^2y}{dt^2} = a\frac{d\omega}{dt} \mp 2\omega v - g\sin\theta. \quad . \quad . \quad . \quad (2)$$

The uppermost sign of the second member in (2) corresponds to the motion away from the lower sign to the motion towards the position of equilibrium of the pendulum (comp. fig. 2 *a* and fig. 2 *b*).

From (1) we get

$$\frac{dx}{dt} = (g\cos\theta + a\omega^2)t + c_1, \quad . \quad . \quad . \quad . \quad (3)$$

$$x = \tfrac{1}{2}(g\cos\theta + a\omega^2)t^2 + c_1 t + c_2. \quad . \quad . \quad (4)$$

At the instant $t = t_0$, *i. e.* the moment at which the particle leaves the nozzle, the relative velocity $\frac{dx}{dt}$ is equal to the velocity v_0 of the jet, which again is determined by

$$v_0 = \sqrt{2h(g + a\omega^2)}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The x-coordinate of the particle is x_0, *i. e.* equal to the distance of the jet-hole from the axis of revolution of the pendulum. From these specifications it follows that $c_1 = v_0$ and $c_2 = 0$. Hence

$$x - x_0 = \tfrac{1}{2}(g\cos\theta + a\omega^2)(t - t_0)^2 + v_0(t - t_0), \quad . \quad (6)$$

while

$$\frac{dx}{dt} = (g\cos\theta + a\omega^2)(t - t_0) + v_0. \quad . \quad . \quad . \quad . \quad (7)$$

In the expression (2), v indicates, as stated above, the the relative velocity of the jet-particle. The expression is based on the assumption that the acceleration $2\omega v$ can be considered perpendicular to the prolonged bar of the pendulum. As a matter of fact, it is perpendicular to the relative path of the jet-particle. If, however, the deflexion θ is sufficiently small, the assumption is justified. Furthermore, we are with small deflexions justified in identifying v with $\frac{dx}{dt}$, and thus get

$$\frac{d^2y}{dt^2} = a\frac{d\omega}{dt} - g\sin\theta \mp 2\omega\,[(g\cos\theta + a\omega^2)(t - t_0) + v_0], \quad (8)$$

wherefrom

$$\frac{dy}{dt} = \left[a\frac{d\omega}{dt} - g\sin\theta \mp 2\omega v_0\right](t-t_0) \mp \omega(g\cos\theta + a\omega^2)(t-t_0)^2 \quad (9)$$

and

$$y = \frac{1}{2}\left[a\frac{d\omega}{dt} - g\sin\theta \mp 2\omega v_0\right](t-t_0)^2 \mp \frac{\omega}{3}(g\cos\theta + a\omega^2)(t-t_0)^3 = \tfrac{1}{2}\mathrm{A}(t-t_0)^2 \mp \frac{\omega}{3}\mathrm{B}(t-t_0)^3, \quad . \quad . \quad . \quad (10)$$

A and B being abbreviations.

If a number of values of $(t-t_0)$ are inserted into (6) and (10), corresponding values of x and y are obtained ; thus the relative path of the particle and hereby the deflexion at a given distance from the nozzle.

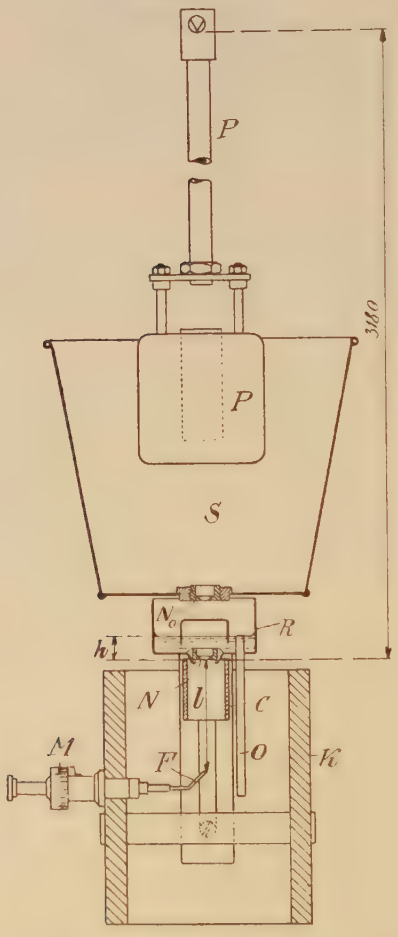
Experimental Verification of the Theory.

In order to verify the theory of the jet attached to a pendulum, the apparatus shown in fig. 3 and fig. 4 was set up. It consisted of a pendulum P, a little more than 3 metres in length and at its lower end furnished with a heavy cast-iron cylinder. To the latter a pail S was attached, during the experiments containing water to a height of some few centimetres. In the bottom of the latter a nozzle N_0 was inserted, and below N_0 a small reservoir R was fastened. In the bottom of R a second nozzle N was fixed. The latter served for the production of the jet used as an accelerometer. Its head was kept constant by means of the overflow O. In order to obtain a steady jet, and especially with the view of avoiding alternations in the direction of the jet during the experiments, the exterior surface of the nozzle was covered with a thin layer of paraffin *. In order to shelter the jet from the resistance of the air during the oscillation of the pendulum, the jet was enclosed in a chamber K which at front and rear was closed with glass panes. Furthermore, the jet was, at its uppermost part, surrounded by a cylinder C. The test of the theory consisted of : (1) a determination of the phase-difference between the jet and the pendulum, and (2) a measurement of the amplitude of the relative

* *Det kgl. danske Videnskab. Selskabs. Meddelelser*, ii. p. 8 (1919), or Phys. Rev. vol. xx. p. 728 (1922).

motion of the jet. Both determinations were, of course, carried out with oscillations of equal size of the pendulum, the amplitude of the latter being controlled by means of the

Fig. 3.

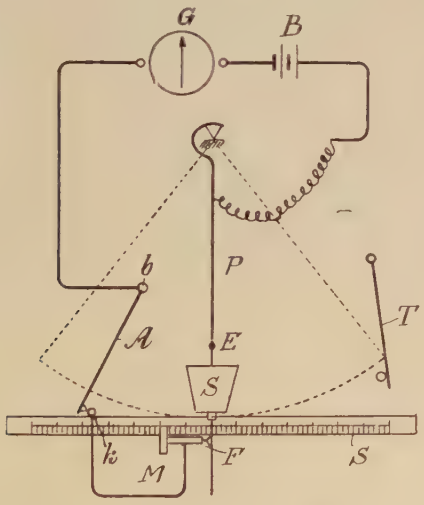


light wire T, fig. 4, against which the pendulum had to hit. The device used for the two determinations (1) and (2) will now be described.

In the side-wall of the chamber K a micrometer M was inserted. By means of the same a contact-piece F could be approached to or removed from the jet. In the diagram

(fig. 4) the micrometer is again indicated as M. In the same figure an electric circuit, containing a galvanometer G and a direct-current source B, is drawn. The circuit, furthermore, contained a contact-piece k which could be moved along the scale S on which the amplitude of the pendulum could be read. On k rested a light arm A which could turn about the horizontal axis b. To the pendulum-rod was fastened a pin E which lifted A from k when the deflexion of the pendulum reached a certain size. Obviously the circuit is only closed when both A has contact with k and the jet at the same time touches F.

Fig. 4.



It is now easily understood how, with this apparatus, the position of the pendulum is found in which the jet passes its zero position. If the contact-piece k has been carried so far out along S that the jet has passed zero and got into touch with F before the pendulum lifts A from k, a deflexion is seen on the galvanometer G at every swing of the pendulum. If, on the other hand, k has been placed so near the middle-point of S that the pendulum breaks the connexion between A and k before the jet passes zero, no deflexion of G will occur. Thus the object of the measurement was to determine the boundary position of k, or, rather, a boundary interval because of the inevitable unsteadiness of the jet. In order to determine the interval,

k was at first adjusted so that a deflexion appeared on G at most swings, and then so that a deflexion occurred only very seldom. The relatively great exactness of the method is illustrated by fig. 5, in which figure the interval is marked. The determination of the amplitude was somewhat simpler than that of the phase-difference. The pin E on the pendulum was removed so that A all the time touched k, and then the micrometer was carried outward until the jet no longer reached F. Actually, in this determination, as in the foregoing, an interval of uncertainty was observed and much in the same way as above. This interval, too, has been introduced into fig. 5.

We now pass on to the calculation, on the basis of the theory of the phase-difference and the amplitude.

The dimensions of the research apparatus (see fig. 3) were:

$$a = 318 \text{ cm.}, \quad h = 2{\cdot}0 \text{ cm.}, \quad l = x - x_0 = 8{\cdot}6 \text{ cm.}$$

The measurements were carried out for an amplitude b, which, read on S (fig. 4), was 65 cm. From a and b the angular amplitude $\vec{\theta}$ of the pendulum was found to be 0·2058. The period of the pendulum being 3·30 sec., the formulæ for its motion were:

$$\theta = 0{\cdot}2058 \sin 1{\cdot}904\, t, \quad . \quad . \quad . \quad . \quad (1)$$

$$\omega = 0{\cdot}3918 \cos 1{\cdot}904\, t, \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{d\omega}{dt} = -0{\cdot}7460 \sin 1{\cdot}904\, t. \quad . \quad . \quad . \quad . \quad (3)$$

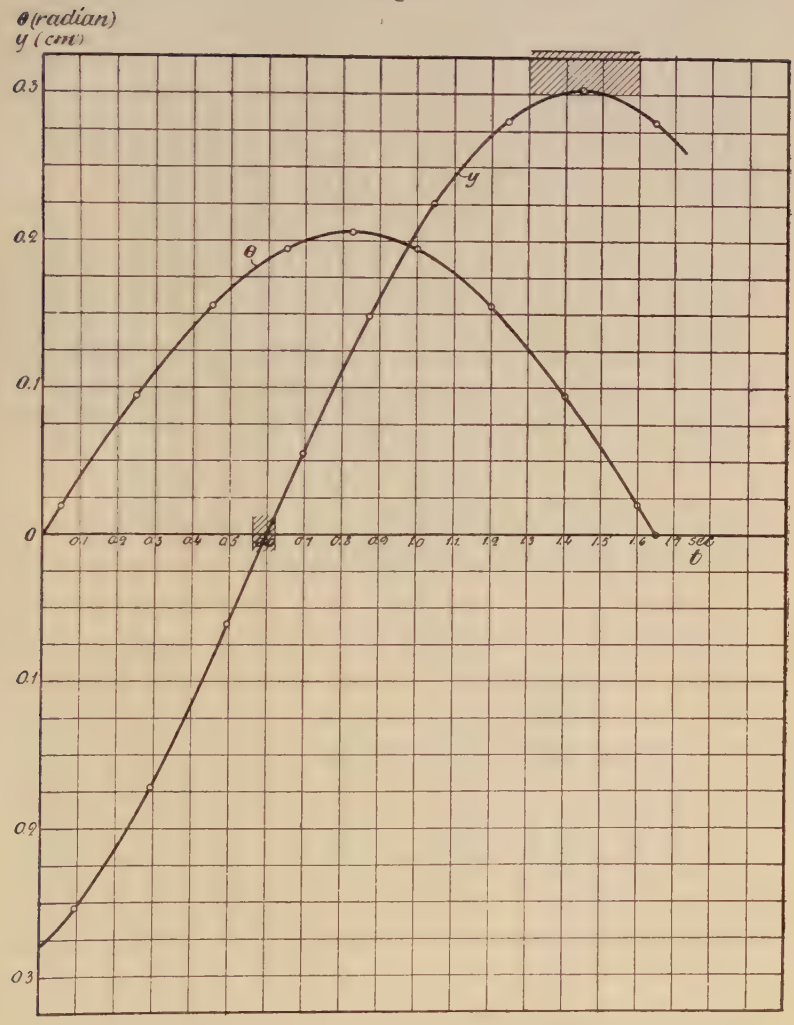
With the view to comparing the results of the experimental test with the theory, a curve representing the variation with the time of the relative deflexion y, measured at the distance of the contact-piece F (fig. 4), was calculated by means of the formula (10), p. 1079. This was done by first determining an approximate value of $t - t_0$, *i. e.* the time for the travelling of the jet-particle from the nozzle to F. The formula used was

$$t - t_0 = -\frac{v_0}{g} + \sqrt{\left(\frac{v_0}{g}\right)^2 + \frac{2l}{g}}, \quad . \quad . \quad . \quad (4)$$

where v_0 was calculated from

$$v_0 = \sqrt{2g(h - \Delta h)}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Fig. 5.



h denoting the counter-pressure of the surface-tension C, given by

$$\Delta h = \frac{2C}{\rho g d}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

ρ being the density of the liquid of the jet and d the diameter of the jet-hole. The latter was in the experimental test

0·25 cm. The surface-tension of water was assumed to be 76 dyne/cm. With these values Δh is found to 0·6 cm. Thus $h-\Delta h=1·4$ cm. and $v_0=52$ cm./sec. Finally, by inserting into (4), the value 0·09 sec. is derived for $t-t_0$. This figure was introduced in the formula (10), and y was then calculated for 9 values of t nearly equally distributed over a half-period of the oscillations of the pendulum. The t-values are entered in the first column of the table below. The θ-, ω-, and $\frac{d\omega}{dt}$-values which were introduced in the formula were those corresponding to $t-0·045$ sec., *i. e.* to the middle-point of the time-interval $t-t_0$ during which the jet-particle moved from the nozzle to F in fig. 4. The values will be found in the second, third, and fourth columns of the table. In the last column but one the exact values for $x-x_0$ have been entered. They are found from formula (6), p. 1078. They deviate, as will be seen, very little from the value 8·6 cm., on which the calculation of y was based. As a matter of fact, the deviations are so small as to allow the values of y in the last column to represent the jet-deflexion at the distance 8·6 cm. from the nozzle.

t.	θ.	ω.	$\frac{d\omega}{dt}$.	B.	$\frac{1}{2}$A.	$x-x_0$.	y.
sec.							
0·095	0·01955	0·3900	0·07087	1030·2	−19·25	9·01	−0·254
0·295	0·09430	0·3482	0·3418	1016·2	−10·47	8·93	−0·171
0·495	0·1555	0·2560	0·5638	991·0	+ 0·04	8·78	−0·061
0·695	0·1945	0·1281	0·7050	968·7	+10·52	8·66	+0·055
0·825	0·2058	0·0000	0·7460	961·3	+18·30	8·61	+0·148
1·045	0·1945	0·1281	0·7050	968·7	+23·99	8·66	+0·225
1·245	0·1555	0·2560	0·5638	991·0	+27·17	8·78	+0·282
1·445	0·09430	0·3482	0·3418	1016·2	+26·76	8·93	+0·303
1·645	0·01955	0·3900	0·07087	1030·2	+22·64	9·01	+0·281

In fig. 5 the relation between y and t has been drawn in the curve y. In the same figure the curve indicating the deflexion θ of the pendulum is introduced in its proper position relative to the y-curve. Finally, as mentioned above, the observed intervals for the zero-point of the y-curve and for the amplitude of the same are introduced.

The agreement between experiment and theory is as perfect as could be expected.

I wish to thank my collaborator Mr. Loegstrup Jensen for his good assistance and The Carlsberg-Fund, Copenhagen, for its contribution, by a grant, to the investigation here considered.

The Royal Technical College,
Physical Laboratory II.,
Copenhagen.
June 1925.

CVIII. *The Doppler Effect in de Sitter's Space-Time. In reply to M. Jean Chazy.* *By* L. Silberstein, *Ph.D.**

IN a previous paper (Phil. Mag. vol. xlviii. 1924, p. 619) I have derived for the Doppler effect, $D=\delta\lambda/\lambda$, for a star and an observer in any inertial motion in de Sitter's space-time the formula [*cf.* (8), (8′), *l. c.*]

$$D+1=\frac{\cos^2\sigma}{\gamma\left[1-\frac{1}{c}\frac{dr}{dt}\sec\sigma\right]} \quad \ldots\ldots \quad (a)$$

$$=\frac{\cos^2\sigma/\gamma}{1\mp\sqrt{1-\frac{\cos^2\sigma}{\gamma^2}\left(1+\frac{p^2}{R^2\sin^2\sigma}\right)}},$$

where $\sigma=r/R$, while γ, p are integration constants determined by (9), *loc. cit.* It was arrived at by developing, without any omissions, the invariant expression $1+D=\frac{ds}{ds'}$, the ratio of corresponding elements of the observer's and the star's world-lines, and it thus can claim rigorous validity.

In a recent note, M. Jean Chazy † expresses the opinion that this formula "would seem inaccurate, since for a source in radial motion, whose velocity vanishes at an instant, it reduces to $D=\cos\sigma-1$ and not to $D=\frac{1}{\cos\sigma}-1$," *i. e.* not to de Sitter's pure distance effect. In fact, for $p=0$, $\beta_m=0$, and $\sigma=\sigma_m$ (minimum distance) formula (a) gives $D=\frac{\cos^2\sigma_m}{\gamma}-1$, and since in this case $\gamma=\cos\sigma_m$, by (9), $D=\cos\sigma_m-1$.

* Communicated by the Author.

† *Comptes Rendus*, Paris, vol. clxxxiii. pp. 1093–1095 (1926). Chazy writes θ instead of our σ.

Now, as is expressly stated on p. 623, $r = R\sigma$ in formula (a) is the distance of the observer from the star at *the instant of observation* or of *receiving* its light. Thus, the star being at its minimum distance (and reversing its motion) at the instant of observation, it manifestly was *approaching* the observer at the instant of emission, as well as during the whole time interval between the emission and the observation. It is, therefore, not at all surprising that the effect in this case is negative or a blue-shift, $D = \cos\sigma - 1$. This removes Chazy's objection. One would expect a de Sitter red-shift $\sec\sigma - 1$ if, e. g., the star and the observer were permanently at relative rest *, which is not the case.

M. Chazy proposes to replace my formula (a) by an apparently different expression, viz. (2), or as rewritten by him on p. 1095 (*l. c*), in our symbols,

$$D + 1 = \frac{\gamma}{\cos^2\sigma}\left(1 + \frac{1}{c}\frac{dr}{dt}\sec\sigma\right). \quad . \quad . \quad . \quad (b)$$

He obtains this formula by combining, after Becquerel, the Doppler effect as it would be expected in homaloidal space-time according to special Relativity with the "field effect" or de Sitter's pure distance effect. Now, such a method does not seem legitimate (since the motion is not uniform, etc.) and, at any rate, is not appropriate to show the invariant character of the expression (b). Yet, as will be shown presently, this expression happens to represent exactly the invariant quotient ds/ds', as does also formula (a). The only difference is that, while in formula (a) r is the distance in the static space of *the star*, i. e. with the origin $r = 0$ placed at the star (*cf.* Phil. Mag., *l. c.*), and at the instant of *observation*, in formula (b) it must be considered as the distance in the static space of the *observer* (origin $r = 0$ at the observer's station) and at the instant of *emission* of the light. Similarly for dr/dt.

In fact, let us repeat our previous reasoning (*l. c.*) but placing this time the origin $r = 0$ at the observing station. We shall thus have the two light-signals:

1st, emitted at the instant t and reaching the observer at the instant α; this will give

$$c(\alpha - t) = \int_0^r \sec\sigma \, . \, dr,$$

where r corresponds to the instant of emission;

* Such will also be the effect if they are at rest only at the instant of *emission*, so that they subsequently recede from each other. This can be seen at once from the alternative form of ds/ds' given below.

2nd, emitted at the instant $t+dt$ and reaching the observer at the instant $\alpha+d\alpha$, so that

$$c(\alpha+d\alpha-t-dt) = \int_0^{r+dr} \sec\sigma \, . \, dr.$$

Hence, subtracting the two equations from each other and noticing that the observer's line-element is now $ds=c\,d\alpha$,

$$ds = cdt\left(1+\frac{1}{c}\frac{dr}{dt}\sec\sigma\right).$$

On the other hand, the corresponding line-element ds' of the star will be determined by the well-known first integral of the equations of a geodesic (inertial motion),

$$\cos^2\sigma \, . \, cdt/ds' = \gamma = \text{const.}$$

Consequently,

$$\frac{ds}{ds'} = \frac{\gamma}{\cos^2\sigma}\left[1+\frac{1}{c}\frac{dr}{dt}\sec\sigma\right],$$

which is the expression (b).

Thus, the formula (b) proposed by Chazy differs from my formula (a) in appearance only. Both formulæ, when interpreted as above, are rigorous. Both represent the same thing, ds/ds', only in different languages, as it were. To state it once more, in (a) the coordinate r and its derivative refer to the static space of the star and to the instant of receiving its light, and in (b) to the static space of the observer and to the instant of emission.

This settles the question.

It is scarcely necessary to add that, so far as astronomical applications are concerned, these subtle distinctions are futile, since the "distances" of remote celestial objects are, in the best case, known to two significant figures only, while v/c is of the order 10^{-3}. Practically, either formula will reduce to the approximate formula

$$D^2 = \left(1-\frac{r_m^2}{r^2}\right)\left(\frac{r^2}{R^2}+\frac{v_m^2}{c^2}\right)$$

given previously. A factor such as $\cos\sigma$ or $\cos^2\sigma$ is, for the time being, hopelessly indiscernible from unity.

At any rate, *both* formulæ hold rigorously, and are equivalent to each other.

Rochester, N.Y.
January 28, 1927.

CIX. *A Generalization of Electrodynamics, consistent with Restricted Relativity and affording a possible explanation of the Earth's Magnetic and Gravitational Fields, and the Maintenance of the Earth's Charge.* *By* W. F. G. Swann, *D.Sc., M.A., A.R.C.S, Professor of Physics and Director of the Sloane Laboratory in Yale University* *.

Abstract.

The electromagnetic equations,

$$\text{(A)}\quad \frac{\rho\mathbf{u}}{c} = -\frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + \operatorname{curl}\mathbf{H}, \qquad \text{(C)}\quad 0 = \frac{1}{c}\frac{\partial \mathbf{H}}{\partial t} + \operatorname{curl}\mathbf{E},$$

$$\text{(B)}\quad \rho = \operatorname{div}\mathbf{E}, \qquad \text{(D)}\quad 0 = \operatorname{div}\mathbf{H},$$

together with a force equation of the form

$$\text{(H)}\quad \left(\mathbf{E} + \frac{[\mathbf{w}.\mathbf{H}]}{c}\right)e = \frac{d}{dt}(m_0 k\mathbf{w}),$$

with $k = \left(1 - \frac{q^2}{c^2}\right)^{-\frac{1}{2}}$ and q the resultant velocity of an electron, are taken as a basis from which to generalize.

The equations corresponding to (A)–(D) are left unchanged for the fields due to negative electricity; but for the fields due to positive electricity they are generalized in the following way:—The 4-vector $\rho\mathbf{u}$, ρic associated with (A) and (B) is replaced by a more general 4-vector $\mathbf{S}$, icS_t, given by

$$\text{(I)}\quad \mathbf{S} = \rho_+\mathbf{u}_+ + \alpha k_+ d\frac{(\rho_+\mathbf{u}_+)}{dt} + \beta k_+ \frac{d}{dt}k_+\frac{d}{dt}(\rho_+\mathbf{u}_+)$$
$$= \rho_+\mathbf{u}_+ + \alpha\mathbf{P} + \beta\mathbf{Q},$$

$$\text{(J)}\quad S_t = \rho_+ + \alpha k_+\frac{d\rho_+}{dt} + \beta k_+\frac{d}{dt}k_+\frac{d\rho_+}{dt} = \rho_+ + \alpha P_t + \beta Q_t,$$

where α and β are invariants of the Lorentzian transformation, and the P's and Q's have the values defined in (I) and (J). The additional terms in (I) and (J) destroy the equations of continuity, the only one appreciably operative in this respect for uniform rotation being $\alpha\mathbf{P}$. By an appropriate choice of α we can make this term give rise to a slow death of positive electricity (amounting to a loss of 0·5 per cent. of the earth's mass in 10^{20} years) such as to leave a continually increasing surplus of negative

* Communicated by the Author. Presented at the American Mathematical Congress, Toronto, August 1924. Also at the Washington Meeting of the American Physical Society, December 29–31, 1924.

which, after building up the necessary electric field, passes off continually, as the atmospheric electric current, by conduction through the atmosphere.

The generalized equations lead, very approximately, to the same expressions for the fields as are given by the classical theory, except that the $\rho_+\mathbf{u}_+$ and ρ_+ of classical theory are replaced by $\mathbf{S}$ and S_t. Thus, in the case of a rotating neutral earth there is a fictitious current density $\alpha\mathbf{P}+\beta\mathbf{Q}$ and a fictitious charge density $\alpha P_t+\beta Q_t$. The value of α chosen as above is too small to make appreciable contribution to the fictitious current density. The fictitious current density is provided for by $\beta\mathbf{Q}$, and the choice of β necessary to result in a magnetic field equal to that of the earth is such that, as regards any fictitious charge density of importance in its power to give rise to the earth's electric field, the term βQ_t is negligible, as is also the term αP_t. The electric field is provided for otherwise, as outlined above.

The forms of the invariants α and β are chosen so that the theory gives the correct ratio for the magnetic field of the earth to that of the sun, and predicts for a small sphere of laboratory size, rotating at the highest attainable speed, a magnetic field and a rate of death of charge which would be immeasurable, or measurable only with considerable difficulty.

Gravitation is provided for by a replacement of the force equation by two equations for the motions of positive and negative electrons respectively, the modification implying, primarily, a difference in the forces between equal like charges and equal unlike charges.

The modifications introduced into the equations of the theory are such that the whole scheme of relations is invariant under the transformation of the restricted theory of relativity.

Introduction.

ANY theory of the earth's magnetic field which invokes the rotation of the earth as a cause will present that field as a function of a, the radius of the sphere, and ω, the angular velocity. A sphere with a current density i of the form $i=\mathrm{AD}\omega^m r^n$, where r is the distance from the axis of rotation and D is the density of the sphere, gives rise to a magnetic field H_z at the pole, given by *

$H_z=\mathrm{AD}\omega^m a^{n+1}\mathrm{F}(n)$, where $\mathrm{F}(n)$ is a function of n only. (1)

* See Appendix, Note 1. We shall relegate to an appendix pieces of analysis and subsidiary discussions which, if included in the main part of the article, would interfere with the continuity of thought.

A large class of theories lead to the equivalent of a current density proportional to $D\omega r$, and so give rise at the surface to a field proportional to $D\omega a^2$. This form of expression has the advantage that on its basis, assuming the magnetic field of the earth to be 0·5 gauss at the earth's pole, we should calculate the known value 50 gauss at the corresponding place on the sun. Moreover, the form of the expression is such as to result in the conclusion that it would be impossible to give to small spheres of laboratory size such angular velocities as would correspond to measurable magnetic fields. These two tests, prediction of the correct ratio of the magnetic fields of the earth and sun, and prediction of a magnetic field of magnitude not, at least, easily measurable in the case of a small sphere set into rotation with high speed, constitute conditions which any theory of terrestrial magnetism must satisfy. Some possibilities which suggest themselves as theories lead to fields at the surface proportional to $D\omega^3 a^2$. This is the case, for example, with those in which the centrifugal force * of the earth's rotation is involved as the primary agency responsible for bringing about conditions which give rise to the field. Quite apart from the fact that such theories, when worked out on any reasonable assumptions, give fields insignificant in absolute values, they would predict for the sun a field much smaller than that of the earth; and for a copper sphere of radius 10 centimetres, rotating at 100 revolutions per second, they would predict for the field at the surface a value over a hundred thousand times that of the earth. This fact is sufficient to rule such theories out of court.

Although a theory giving rise to a real or apparent current density of the form $D\omega r$ satisfies the conditions well as regards comparison with the field of the sun and that of a small body rotating at high speed, it will turn out that such a theory is unsatisfactory for other reasons. In the first place it makes the effective current density at an element of matter proportional to its linear velocity, and otherwise independent of its angular velocity, so that such theories would presumably lead, or at any rate suggest, in general, magnetic fields as a result of the translation of matter with uniform rectilinear velocity, a consequence which would lead to undesirable conclusions as regards magnetic fields due to the translatory motion of the planets, and which has, moreover, been demonstrated as non-existent by the experiments

* See W. F. G. Swann, "On the Magnetic Electric Fields which spontaneously arise in the Vicinity of a Rotating Conducting Sphere," Terr. Mag. vol. xxii. p. 154 (1917).

of H. A. Wilson *. Moreover, as we shall see later, if we attempt to correlate in a rational way, under a scheme of modified electrodynamics, a situation in which neutral matter can by its motion give rise to a magnetic field according to the same law as that which in classical theory governs the magnetic field due to moving electricity, we shall evolve the unwelcome conclusion that what we desire to regard as neutral matter will also give rise to an electric field. Even though our definitions may have been formulated in such a way that the matter may be regarded technically as neutral, the analysis will refuse to be deceived by our devices, and in giving us our magnetic field due to the rotation of neutral matter, it will make that "neutral matter" present us with an electric field as large as the field we should have obtained in classical electrodynamics, if we had imagined the magnetic field produced by the rotation of a charged earth.

If we could provide for an apparent current density proportional to $D\omega^4 r^3$, the magnetic field at the surface of the sphere would come out proportional to $D\omega^4 a^4$, as may be seen from (1) : and, within the limits of the experimental data, an expression of this form would serve almost as well as one of the form $D\omega a^2$, cited above, for the purpose of giving the correct ratio of the magnetic fields of the earth and sun †. For a sphere of 10 cm. radius and with the earth's density rotating 100 times per second, it would give at the surface on the pole a magnetic intensity $3{\cdot}4\times10^{-4}$ of the corresponding intensity for a sphere of the earth's size rotating with the earth's angular velocity. A field amounting to $3{\cdot}4\times10^{-4}$ of the earth's intensity is not inconceivably beyond the limits of experimental detection ; but the difficulty of detecting it would be very great when the high angular velocity associated with its production is taken into account.

Of all possible expressions of a form proportional to D and to integral powers of ω and r for the apparent current density at a distance r from the axis of rotation, that proportional to $D\omega^4 r^3$ is the only one, other than the expression ‡ $D\omega r$, which would be in harmony with the relative magnetic fields of the sun and earth and with the smallness of the magnetic field to be obtained by the rotation of a small body at high speed. For comparison of the fields of the sun and earth would necessitate that in any additional factor $\omega^m r^n$

* See H. A. Wilson, Proc. Roy. Soc. vol. civ. pp. 451–455 (1923).

† In fact the ratio of $\omega^3 a^2$ for the sun to that for the earth is equal to 1/1·5, and is thus not very far different from unity.

‡ The objections to which have already been discussed.

which we might attach to $D\omega^4 r^3$, m would be greater than n, while the avoidance of production of an unallowably large magnetic field for a small body rotating at high speed of, say, 1000 revolutions per second would necessitate $m \leq n$.

In Table I. are collected a few figures illustrating the foregoing remarks, and giving, for various types of law as to the variation of apparent current density with r and ω, the relative values of the magnetic intensity H_z at the pole for the cases of the sun, the earth, and a sphere of the earth's density, but of radius 10 cm., rotating at 100 revolutions per second. The relative values of a, ω, and $\omega^3 a^2$ are also given. The significance attaching to the quantity J will appear later.

TABLE I.

	Relative Values.			
	S	E	100 rev./sec. Radius 10 cm.	Remarks.
a	$7{\cdot}0\times10^{5}$	$6{\cdot}4\times10^{3}$	1	
ω	1	25·5	$2{\cdot}2\times10^{2}$	
$\omega^3 a^2$	1	1·4	$2{\cdot}2\times10^{5}$	
H_z	58	0·5	$1{\cdot}0\times10^{-9}$	$i \propto Dr\omega$; $H_z \propto D\omega a^2$.
H_z	0·1	0·5	$7{\cdot}8\times10^{4}$	$i \propto Dr\omega^2$; $H_z \propto D\omega^3 a^2$.
H_z	42	0·5	$1{\cdot}7\times10^{-4}$	$i \propto Dr^3\omega^4$; $H_z \propto D\omega^4 a^4$.
J	-15×10^{14}	-3×10^{12}	$-0{\cdot}85\times10^{3}$	$J \propto D\omega^2 a^3$.
J	-4×10^{16}	-3×10^{12}	$-1{\cdot}0\times10^{-4}$	$J \propto D\omega a^3$.

In the theory which will subsequently be developed, we shall consequently provide for the equivalent of a current density of the form $\omega^3 r^2$. This will have the advantage of making the current density depend on ω explicitly as well as on the linear velocity (ωr), and will be of the type to give zero result for non-rotational motion. Of course it must be understood that, when the term giving rise to this apparent current density finally appears in the theory and equations to be developed, it will come in in a more general form as applicable to all kinds of motion, and in such a way as to make it part of a consistent theory of electrodynamics. All that we desire to state here is our intention to adjust the

general theory in such a way as to reduce for the special case of uniform rotation to a condition of this type.

It must be pointed out that all theories of the kind under consideration lead in their simplest aspects to a state of magnetization symmetrical about the axis of rotation. It is felt that, once a satisfactory theory providing for this condition is developed, the difficulties inherent in accounting for the non-coincidence of the magnetic and geographic axes, and the departure of the field from that of the types following from an effective current density which is a function only of r, might well be of secondary seriousness.

As regards the maintenance of the earth's charge, the facts are these. The earth is negatively charged to an extent such as to give rise to a potential gradient of about 150 volts per metre. That charge is streaming out from the earth on account of the atmospheric conductivity at such a rate that 90 per cent. of it would be gone in ten minutes if there were no means of replenishing the loss. The difficulties in explaining the replenishment in a manner such as to maintain consistency with all the facts are very great *, and, while theories have been proposed, all have their objections. So serious is the situation that Dr. G. C. Simpson † has been moved to raise the question of whether or not charge may be spontaneously generated in the earth's interior. Such a view must of course be moulded with the greatest care into any logical theory, as one is here striking at the very foundations of the fundamental concepts of electric charge, and to tamper with the structure here may throw complete confusion into the most commonplace electrodynamic conclusions everywhere. Nevertheless, in the theory about to be developed, the endeavour has been made to invoke the spirit of this idea of creation (or annihilation) of charge as a result of the earth's motion, but to do so in a manner in which its effect on the whole of the remainder of the electrodynamic scheme is perfectly precise and logically understandable. Speaking briefly, the effect becomes secured by making the modified electrodynamic equations of a type in which the equation of continuity no longer holds universally, at least for positive electricity. Under these conditions the rotation of the earth is made to give rise to a slow death of positive electricity, so that the earth charges

* See, for example, W. F. G. Swann, "Unsolved Problems of Cosmical Physics," Journal of the Franklin Institute, vol. cxcv. pp. 433-474 (1923).

† G. C. Simpson, "Some Problems of Atmospheric Electricity," Monthly Weather Review, vol. xliv. p. 121 (1916).

negatively to such an extent that a steady state is finally attained when the conduction through the atmosphere into space balances the death of positive electricity. It turns out that it is only necessary to provide for a rate of death of positive electricity corresponding to a disappearance of half of one per cent. of the earth's mass in 10^{20} years, a death corresponding to the loss of one proton per c.c. per day.

Here we have no knowledge of the electric field of another planet to guide us in determining the way in which the field is to depend on the angular velocity and radius. We are, however, able to restrict our choice by the fact that the theory must not lead to the conclusion that the generation of charge by a small body rotating at high speed in the laboratory shall be easily measurable.

The modification introduced in the electromagnetic scheme to account for gravity is almost precisely that of the theory of Lorentz, in which the basic idea is the assumption of a difference between the force of attraction between unlike charges and the force of repulsion between corresponding like charges. The only reason for including this theory in the present paper is the desire to mould the gravitational theory into harmony with the others in such a manner as to result in one complete scheme for the whole, a scheme, moreover, of a form invariant under the transformation of the restricted theory of relativity.

Generalization of the Electrodynamic Equations.

Remarks on the Classical Scheme.

The classical circuital relations of electrodynamics are, in the usual notation, and in Heavisidean units,

$$\frac{\rho \mathbf{u}}{c} = -\frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + \operatorname{curl} \mathbf{H}, \quad . \quad . \quad . \quad . \quad (2)$$

$$\rho = \operatorname{div} \mathbf{E}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$0 = \frac{1}{c}\frac{\partial \mathbf{H}}{\partial t} + \operatorname{curl} \mathbf{E}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$0 = \operatorname{div} \mathbf{H}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

These equations give the fields $\mathbf{E}$ and $\mathbf{H}$ when ρ and $\mathbf{u}$ are assigned, but they do not determine the motion of the electricity itself. This is provided for by a fifth relation

not derivable from (2)–(5). This equation may be written

$$\left(\mathbf{E}+\frac{[\mathbf{wH}]}{c}\right)e=\frac{d}{dt}\frac{m_0\mathbf{w}}{\left(1-\frac{q^2}{c^2}\right)^{\frac{1}{2}}}+\mathbf{B}, \quad . \quad . \quad (6)$$

where $\mathbf{E}$, $\mathbf{H}$ is the field at some specified point inside the electron, neglecting the field of the electron itself, and where e is the electronic charge, $\mathbf{w}$ the electron's vector velocity and q its resultant velocity, m_0 the rest mass, viz. $e^2/6\pi ac^2$, with a the electronic radius, and where $\mathbf{B}$ is the radiation reaction.

Precision of statement demands that we say something more about this equation; but as the points involved have no direct bearing upon the generalization of the whole set of equations which we intend to discuss, and have to do primarily with the classical theory as such, we shall relegate remarks in this connexion to the Appendix, Note 2.

Now it is desirable that we note several points with regard to equations (2)–(6). These are:

(*a*) Equations (2)–(5) are capable of being solved, and give $\mathbf{E}$ and $\mathbf{H}$ in the form

$$\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{U}}{\partial t}-\operatorname{grad}\phi, \quad . \quad . \quad . \quad . \quad (7)$$

$$\mathbf{H}=\operatorname{curl}\mathbf{U}, \quad . \quad . \quad . \quad , \quad . \quad . \quad . \quad . \quad (8)$$

where

$$4\pi\phi=\iiint\frac{[\rho]}{\mathrm{R}}\,d\tau, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$4\pi c\mathbf{U}=\iiint\frac{[\rho\mathbf{u}]}{\mathrm{R}}\,d\tau, \quad . \quad . \quad . \quad . \quad (10)$$

ϕ and $\mathbf{U}$ being restricted by the relation

$$\operatorname{div}\mathbf{U}=-\frac{1}{c}\frac{\partial\phi}{\partial t}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

the square brackets here being used to denote that the potentials are calculated in the usual retarded sense. It thus results that each element of electricity produces its own contribution to the field at a point, these contributions being additive to obtain the resultant field. Thus, if we should so wish, we could speak of the field $\mathbf{E}_+$, $\mathbf{H}_+$ produced by positive electricity and of the field $\mathbf{E}_-$, $\mathbf{H}_-$ produced by negative electricity.

(*b*) Equations (2) and (3) contain, as a direct algebraical consequence, the equation

$$-\frac{\partial \rho}{\partial t} = \operatorname{div} \rho \mathbf{u}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This is the equation of continuity, and provides for the conservation of electric charge. It may not be inappropriate to recall that the equation of continuity is not something which can be provided for other than through the equations. It is not true for everything. It is not true of the people in this country that the rate of decrease of population is equal to the difference between the rates at which people go out of and come into the country, because some are born here and some die here. Equation (12) denies the possibility of electricity being born or dying in the volume elements, and (11), which is implied by it (see Appendix, Note 4), serves to restrict the values of ρ and $\rho\mathbf{u}$ assigned in our problems to those in harmony with it.

(*c*) An analysis of the steps by which (7)–(11) are derived from equations (2)–(5) will show that ρ and $\rho\mathbf{u}$ occur as they do in the solutions for $\mathbf{E}$ and $\mathbf{H}$ *not* because they happen to be density and density times velocity, but because they constitute the left-hand sides of equations (2) and (3). In other words, consider a set of equations

$$\frac{\mathbf{S}}{c} = -\frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + \operatorname{curl} \mathbf{H}, \quad . \quad . \quad . \quad . \quad (13)$$

$$S_t = \operatorname{div} \mathbf{E}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$0 = \frac{1}{c}\frac{\partial \mathbf{H}}{\partial t} + \operatorname{curl} \mathbf{E}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$0 = \operatorname{div} \mathbf{H}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where $\mathbf{S}$ is any vector with components S_x, S_y, S_z, and S_t is a scalar satisfying *

$$-\frac{\partial S_t}{\partial t} = \operatorname{div} \mathbf{S}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The solution of these equations is

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{U}}{\partial t} - \operatorname{grad} \phi, \quad . \quad . \quad . \quad . \quad (18)$$

$$\mathbf{H} = \operatorname{curl} \mathbf{U}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

* The subscript t is used merely to call to mind the association of the fourth component with the t-axis in the sense understood in the restricted theory of relativity.

where
$$4\pi\phi = \iiint \frac{[S_t]}{R} d\tau; \quad 4\pi c\mathbf{U} = \iiint \frac{[\mathbf{S}]}{R} d\tau, \qquad (20)$$

with ϕ and $\mathbf{U}$ subject to the condition

$$\operatorname{div}\mathbf{U} = -\frac{1}{c}\frac{\partial\phi}{\partial t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

This fact is proved formally in Appendix, Note 3.

Equation (17) is an analytical consequence of (13) and (14), and, whatever $\mathbf{E}$ and $\mathbf{H}$ may be, it is a condition automatically imposed on S_x, S_y, S_z, S_t by the mere fact of their being equated to the right-hand sides of (13) and (14). It is the representative of equation (12) in the classical equations, and equation (21) has merely the function of preventing us from assigning, in any problem, values of $\mathbf{S}$ and S_t which would themselves violate (17), just as (11) prevents us from assigning values of ρ and $\mathbf{u}$ which would themselves violate the equation of continuity (12), an equation which forms part of the basis of solution of the problem (see Appendix, Note 4). Of course (17) is no longer the equation of continuity except for the special case

$$\mathbf{S} = \rho\mathbf{u}, \quad S_t = \rho.$$

(*d*) With a proper understanding of the meanings of $\mathbf{E}$ and $\mathbf{H}$, an understanding provided, for example, in the definition of these quantities which follows from limiting cases of (6), the whole set of equations (2)–(6) is invariant (see Note 5) under the transformation of the restricted theory of relativity, viz.

$$x' = \epsilon(x - vt), \quad y' = y, \quad z' = z, \quad t' = \epsilon\left(t - \frac{v}{c^2}x\right), \qquad (22)$$

where
$$\epsilon = \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}.$$

The invariance of (2)–(5) follows from the following facts. In the sense of their proper definitions, H_x, H_y, H_z, $-iE_x$, $-iE_y$, $-iE_z$ constitute a 6-vector (i being $\sqrt{-1}$), so that the four quantities formed by the three components of the right-hand side of (2) and the right-hand side of (3), with an additional factor i, constitute a 4-vector. Moreover, the three components of $\rho\mathbf{u}/c$, together with the quantity ρ (with an i attached), form the four components of a 4-vector. Again, the three components of the right-hand side of (4) and the right-hand side of (5), with a factor i, constitute the four components of another 4-vector; while, as regards (6), after multiplying throughout by $(1-q^2/c^2)^{-\frac{1}{2}}$, the left-hand side corresponds to three of the four components of a 4-vector, and the right-hand side, if properly chosen as regards B,

corresponds also to three of the four components of a 4-vector in the same direction.

Thus, in order to maintain invariance under the restricted theory of relativity in the case of such a set of equations as (13)–(16), all that is necessary is to provide, as corresponding to (6), a fifth equation which will lead to definitions of $\mathbf{E}$ and $\mathbf{H}$ such as to make $\mathbf{H}$, $-i\mathbf{E}$ a 6-vector, and to choose the quantities S_x, S_y, S_z, icS_t so that they form the four components of a 4-vector satisfying the relation (17).

The Generalization.

In proceeding to a generalization of the equations in line with the possibilities pointed out in (*c*) and (*d*), we first write down two sets of circuital relations of the classical type—one for the field due to positive electricity, and the other for the field due to negative electricity. It is the former set which we shall generalize, leaving the latter in its old form. We shall denote by subscripts + or — fields produced by or quantities associated with positive or negative electricity respectively.

For the positive electricity we shall generalize equations (2)–(5) by replacing $\rho\mathbf{u}$, ρ by $\mathbf{S}_+$, $(S_t)_+$, as in (*c*), where

$$\mathbf{S}_+ = \rho_+\mathbf{u}_+ + \alpha\mathbf{P} + \beta\mathbf{Q}, \quad . \quad . \quad . \quad . \quad (23)$$

$$(S_t)_+ = \rho_+ + \alpha P_t + \beta Q_t, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where P_x, P_y, P_z, icP_t constitute components of a 4-vector, Q_x, Q_y, Q_z, icQ_t constitute the components of another 4-vector, $(\rho_+u_+)_x$, $(\rho_+u_+)_y$, $(\rho_+u_+)_z$, $ic\rho_+$ constitute the components of another 4-vector, and α and β are invariants of the Lorentzian transformation.

Our complete set of circuital relations then becomes

$$\frac{\mathbf{S}_+}{c} = -\frac{1}{c}\frac{\partial\mathbf{E}_+}{\partial t} + \operatorname{curl}\mathbf{H}_+, \quad . \quad . \quad . \quad (25)$$

$$(S_t)_+ = \operatorname{div}\mathbf{E}_+, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$0 = \frac{1}{c}\frac{\partial\mathbf{H}_+}{\partial t} + \operatorname{curl}\mathbf{E}_+, \quad . \quad . \quad . \quad . \quad (27)$$

$$0 = \operatorname{div}\mathbf{H}_+, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$\frac{(\rho_-\mathbf{u}_-)}{c} = -\frac{1}{c}\frac{\partial\mathbf{E}_-}{\partial t} + \operatorname{curl}\mathbf{H}_-, \quad . \quad . \quad . \quad . \quad (29)$$

$$\rho_- = \operatorname{div}\mathbf{E}_-, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

$$0 = \frac{1}{c}\frac{\partial\mathbf{H}_-}{\partial t} + \operatorname{curl}\mathbf{E}_-, \quad . \quad . \quad . \quad . \quad (31)$$

$$0 = \operatorname{div}\mathbf{H}_-, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where $\mathbf{S}_+$, $(S_t)_+$ are given by (23) and (24).

It is, however, necessary to add to these a force equation, and an equation, moreover, which will provide for the 6-vector characteristics of the vectors $\mathbf{H}_+$, $-i\mathbf{E}_+$ and $\mathbf{H}_-$, $-i\mathbf{E}_-$. As a matter of fact, we shall write down two force equations—one for the motion of positive and one for the motion of negative electrons. These we shall write as follows:—

$$\frac{m_+}{e_+}\frac{d}{dt}(k_+\mathbf{w}_+) = \mathbf{E}_+ + \frac{[\mathbf{w}_+\mathbf{H}_+]}{c} + \lambda\left(\mathbf{E}_- + \frac{[\mathbf{w}_+\mathbf{H}_-]}{c}\right), \quad (33)$$

$$\frac{m_-}{e_-}\frac{d}{dt}(k_-\mathbf{w}_-) = \mathbf{E}_- + \frac{[\mathbf{w}_-\mathbf{H}_-]}{c} + \lambda\left(\mathbf{E}_+ + \frac{[\mathbf{w}_-\mathbf{H}_+]}{c}\right), \quad (34)$$

where

$$k_+ \equiv \left(1-\frac{q_+^2}{c^2}\right)^{-\frac{1}{2}}; \quad k_- \equiv \left(1-\frac{q_-^2}{c^2}\right)^{-\frac{1}{2}}, \quad . \quad (35)$$

q_+ and q_- being the absolute velocities and $\mathbf{w}_+$ and $\mathbf{w}_-$ the vector velocities of the positive and negative electrons respectively. The factor λ is a constant very nearly equal to unity; and, in its difference from unity, it provides for a difference in the motional effect of unit field on an electron according as that field is produced by positive or negative electricity. It is to the factor λ that we shall look later for the explanation of gravitation.

Now, by taking the scalar product of $\mathbf{w}_+$ and each side of (33), we readily derive

$$\frac{m_+}{e_+}\left(\mathbf{w}_+ \cdot \frac{d}{dt}k_+\mathbf{w}_+\right) = (\mathbf{E}_+ \cdot \mathbf{w}_+) + \lambda(\mathbf{E}_- \cdot \mathbf{w}_+), \quad (36)$$

and in an analogous way from (34) we derive

$$\frac{m_-}{e_-}\left(\mathbf{w}_- \cdot \frac{d}{dt}k_-\mathbf{w}_-\right) = (\mathbf{E}_- \cdot \mathbf{w}_-) + \lambda(\mathbf{E}_+ \cdot \mathbf{w}_-). \quad (37)$$

$k_+\dfrac{d}{dt}(k_+\mathbf{w}_+)$, $\dfrac{k_+ i}{c}\left(\mathbf{w}_+ \cdot \dfrac{d}{dt}k_+\mathbf{w}_+\right)$ constitute a 4-vector,

as do also the corresponding quantities with negative subscripts. It is shown in Appendix (Note 5) that with the definitions of $\mathbf{E}_+$, $\mathbf{E}_-$, $\mathbf{H}_+$, $\mathbf{H}_-$, appropriate to the solution, $\mathbf{H}_+$, $-i\mathbf{E}_+$ and $\mathbf{H}_-$, $-i\mathbf{E}_-$ constitute 6-vectors, so that the whole set of equations (25)–(37) is invariant.

A further remark must be added to the effect that equations (33) and (34), although generalized from the classical force equation in one sense, appear to have lost generality in another sense in that the kinetic reaction represented by the left-hand side contains no terms involving higher time

derivatives of the velocity than the first. This restriction is by no means essential, however, for, remembering that we may from any 4-vector obtain another by operating with $k_+\frac{d}{dt}$, it is obvious that we could generalize the left-hand side of (33), for example, to

$$\frac{1}{k_+}\left\{ak_+\frac{d}{dt}k_+\frac{d}{dt}(k_+\mathbf{w}_+)+bk_+\frac{d}{dt}k_+\frac{d}{dt}k_+\frac{d}{dt}(k_+\mathbf{w}_+)+\ldots \text{etc.}\right\}, \quad . \quad . \quad . \quad (38)$$

where a, b ... etc. are invariants. We could even insert invariants under the operators $\frac{d}{dt}$ without destroying the 4-vector character of the expression. Further, as far as relativity is concerned, the invariants are arbitrary except for the restriction that if $\mathbf{W}$ represents the first three of the components of the 4-vector, the fourth must be equal to $k_+i(\mathbf{W}.\mathbf{w})/c$, as pointed out in Appendix (Note 6) Analogous remarks apply, of course, to equation (34).

This matter concerned with generalizations of the left-hand side of (33) and (34) plays, of course, no part in the applications to terrestrial magnetism, terrestrial electricity, and gravitation discussed in this paper, and it is introduced merely as part of the discussion of the whole scheme of generalized electrodynamics.

In a rather complex situation of the kind here involved, it is desirable that one pay proper attention to the definitions of the quantities one uses—such quantities as m, e, etc. We shall not introduce an interruption by discussing these matters here, but shall relegate them to the Appendix (Note 7).

We must now return to the equations (23) and (24) and the circuital relations (25)–(32). We understand these relations as applying generally for any kind of motion, but it will be our purpose to adjust $\mathbf{P}$, P_t, $\mathbf{Q}$, Q_t, α and β so that for uniform rotation they give us the results we hope for in that case. Our equations for $\mathbf{E}$ and $\mathbf{H}$ will then be as follows:—

$$\mathbf{E}_+ = -\operatorname{grad}\phi_+ - \frac{1}{c}\frac{\partial \mathbf{U}_+}{\partial t}, \quad . \quad . \quad . \quad (39)$$

$$\mathbf{H}_+ = \operatorname{curl}\mathbf{U}_+, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$\mathbf{E}_- = -\operatorname{grad}\phi_- - \frac{1}{c}\frac{\partial \mathbf{U}_-}{\partial t}, \quad . \quad . \quad . \quad (41)$$

$$\mathbf{H}_- = \operatorname{curl}\mathbf{U}_-, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

where

$$4\pi\phi_+ = \iiint \frac{[\rho_+ + \alpha P_t + \beta Q_t]}{R}\, d\tau, \quad . \quad . \quad (43)$$

$$4\pi c\mathbf{U}_+ = \iiint \frac{[\rho_+\mathbf{u}_+ + \alpha\mathbf{P} + \beta\mathbf{Q}]}{R}\, d\tau, \quad . \quad (44)$$

$$4\pi\phi_- = \iiint \frac{[\rho_-]}{R}\, d\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

$$4\pi c\mathbf{U}_- = \iiint \frac{[\rho_-\mathbf{u}_-]}{R}\, d\tau. \quad . \quad . \quad . \quad . \quad . \quad (46)$$

With the understanding that, on account of (17),

$$-\frac{\partial\rho_+}{\partial t} - \frac{\partial}{\partial t}(\alpha P_t) - \frac{\partial}{\partial t}(\beta Q_t) = \operatorname{div}\rho_+\mathbf{u}_+ + \operatorname{div}(\alpha\mathbf{P}) + \operatorname{div}(\beta\mathbf{Q}), \quad (47)$$

just as, on account of the analogous equation for the unmodified scheme for negative charges,

$$-\frac{\partial\rho_-}{\partial t} = \operatorname{div}\rho_-\mathbf{u}_-. \quad . \quad . \quad . \quad . \quad . \quad (48)$$

As already remarked (see Appendix, Note 4), (47) and (48) are the equivalent of the restricting relations:

$$\operatorname{div}\mathbf{U}_+ = -\frac{1}{c}\frac{\partial\phi_+}{\partial t}, \quad . \quad . \quad . \quad . \quad . \quad (49)$$

$$\operatorname{div}\mathbf{U}_- = -\frac{1}{c}\frac{\partial\phi_-}{\partial t}. \quad . \quad . \quad . \quad . \quad . \quad (50)$$

Now (47) is no longer the equation of continuity. In other words, it is no longer true that $-\partial\rho_+/\partial t$ is represented by the net rate at which positive electricity goes *out* of the unit of volume. The equation provides for a true birth or death of positive electricity on account of the additional terms in it. The rate of death of charge density is $\frac{-\partial\rho_+}{\partial t}$, where, since $\operatorname{div}\rho_+\mathbf{u}_+$ is zero for uniform rotation of a homogeneous sphere,

$$-\frac{\partial\rho_+}{\partial t} = \operatorname{div}(\alpha\mathbf{P}) + \operatorname{div}(\beta\mathbf{Q}) + \frac{\partial}{\partial t}(\alpha P_t) + \frac{\partial}{\partial t}(\beta Q_t), \quad (51)$$

an expression which we shall have occasion to use presently.

Again, if for a piece of neutral matter $\rho_+ = -\rho_-$, and if

$\mathbf{u}_+ = \mathbf{u}_-$, we obtain for this case, by addition from (43) and (45) and by addition from (44) and (46),

$$4\pi(\phi_+ + \phi_-) = \iiint \frac{[\alpha \mathrm{P}_t + \beta \mathrm{Q}_t]}{\mathrm{R}} d\tau, \quad . \quad . \quad (52)$$

$$4\pi c(\mathbf{U}_+ + \mathbf{U}_-) = \iiint \frac{[\alpha \mathbf{P} + \beta \mathbf{Q}]}{\mathrm{R}} d\tau, \quad . \quad . \quad (53)$$

and the value of $\mathbf{E}_+ + \mathbf{E}_-$ and $\mathbf{H}_+ + \mathbf{H}_-$ may be obtained directly from these by the aid of (39)–(42). In fact

$$\left.\begin{aligned} \mathbf{E}_+ + \mathbf{E}_- &= -\operatorname{grad}(\phi_+ + \phi_-) - \frac{1}{c}\frac{\partial}{\partial t}(\mathbf{U}_+ + \mathbf{U}_-); \\ \mathbf{H}_+ + \mathbf{H}_- &= \operatorname{curl}(\mathbf{U}_+ + \mathbf{U}_-). \end{aligned}\right\} \quad (54)$$

It is of course true that these quantities are not strictly to be regarded as the electric and magnetic fields which would figure in a practical measurement for the cases under consideration. They differ from these on account of the difference between unity and the λ of equations (33)–(34); and, in view of the fact that the whole of the enormous amounts of positive and negative electricity in the earth participate separately in the determination of ϕ_+, $\mathbf{U}_+$ and ϕ_-, $\mathbf{U}_-$, it is not obvious that the small difference between λ and unity is of negligible account. It turns out that the magnitude of the gravitational constant is such as to justify the approximation, however, as is shown in the Appendix (Note 8); so that while it is not necessary to make any approximation at all, we shall do so in order to avoid complications of the expressions to the obscuration of the main ideas.

Choice of the quantities $\mathbf{P}$, P_t; $\mathbf{Q}$, Q_t.

Returning to equations (23) and (24), where $\mathbf{P}$, P_t; $\mathbf{Q}$, Q_t first made their appearance as generalization on the terms $\rho_+ \mathbf{u}_+$, ρ_+, and remembering that by operating successively with $k_+ \dfrac{d}{dt}$ on the 4-vector $\rho_+ \mathbf{u}_+$, $\rho_+ ic$ we obtain a set of 4-vectors of successively increasing orders, it seems natural to take the first two of these as corresponding to the 4-vectors $\mathbf{P}$, $ic\mathrm{P}_t$; $\mathbf{Q}$, $ic\mathrm{Q}_t$ respectively; so that on this basis

we have

$$\mathbf{P} = k_+ \frac{d}{dt}(\rho_+ \mathbf{u}_+) = k_+ \rho_+ \dot{\mathbf{u}}_+ + k_+ \mathbf{u}_+ \frac{d\rho_+}{dt} \quad . \quad . \quad . \quad (55)$$

$$P_t = k_+ \frac{d\rho_+}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

$$\mathbf{Q} = k_+ \frac{d}{dt} k_+ \frac{d}{dt}(\rho_+ \mathbf{u}_+) = k_+^2 \rho_+ \ddot{\mathbf{u}}_+ + 2k_+^2 \dot{\mathbf{u}}_+ \frac{d\rho_+}{dt} + k_+^2 \mathbf{u}_+ \frac{d^2\rho_+}{dt^2} \quad . \quad (57)$$

$$Q_t = k_+ \frac{d}{dt} k_+ \frac{d\rho_+}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

By this device we generalize the $\rho\mathbf{u}$ of classical theory to an expression involving terms in $\dot{\mathbf{u}}$, $\ddot{\mathbf{u}}$, a generalization which fits in with one's intuitions as to the proper fitness of things; and yet we do this in a manner which retains harmony with the restricted theory of relativity. Indeed, it is possible to generalize the expressions for $\dot{\mathbf{S}}_+$, $(S_t)_+$ of equations (23) and (24) still further by the addition of 4-vector terms of higher orders, and to do this without adding materially to the complexity of the theory. We shall, however, content ourselves with two terms.

For uniform rotation, and in view of the fact that $k_+ = (1 - q_+^2/c^2)^{-\frac{1}{2}}$ is constant with the time, equations (55)–(58) become, in terms of the distance r from the axis of rotation and the angular velocity ω,

$$\mathbf{P} = -k_+ r\omega^2 \rho_+, \quad . \quad . \quad . \quad . \quad . \quad (59)$$

$$P_t = k_+ \frac{d\rho_+}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

$$\mathbf{Q} = k_+^2 r\omega^3 \rho_+, \quad . \quad . \quad . \quad . \quad . \quad (61)$$

$$Q_t = k_+^2 \frac{d^2\rho_+}{dt^2}, \quad . \quad . \quad . \quad . \quad . \quad (62)$$

where we have neglected the terms involving $d\rho_+/dt$ and $d^2\rho_+/dt^2$ in equations (55) and (57) in comparison with the first terms on the right-hand sides of these equations. This approximation involves neglecting quantities of the order $\dot{\rho}_+/\rho_+\omega$ and $\ddot{\rho}_+/\rho_+\omega^2$ compared with unity. Now, although one of the purposes of the generalization discussed in this paper is to secure a finite value of $d\rho_+/dt$ to provide for the atmospheric electric current, it turns out that the value of $d\rho_+/dt$ necessary is such that $\dot{\rho}_+/\rho_+ = -1{\cdot}7 \times 10^{-30}$, so that

since $\omega = 7{\cdot}3 \times 10^{-5}$, for the earth, the quantity $\dot{\rho}_+/\rho_+\omega$ is quite negligible compared with unity. Again, even though $\ddot{\rho}$ were so large that $\dot{\rho}$ changed by 100 per cent. in one second, $\ddot{\rho}_+/\rho_+\omega^2$ would only amount to a quantity of the order 3×10^{-22}, and would be negligible compared with unity. As a matter of fact, our theory will provide for a constant value of $\dot{\rho}^+$.

In applying these expressions in (52) and (53) we should, strictly speaking, observe that the potentials are retarded, as indicated. However, in view of the uniformity of the rotation the retarded potentials only differ from the unretarded ones in virtue of such change of the numerators with time as results from the slow death of positive electricity provided for by (51), and the effect of neglecting the retarded feature is insignificant (see Appendix, Notes 9 and 10). The extreme closeness of approximation to a steady state also renders insignificant the contribution

$$-\frac{1}{c}\frac{\partial}{\partial t}(\mathbf{U}_+ + \mathbf{U}_-) \text{ to } \mathbf{E}_+ + \mathbf{E}_-,$$

as given by (54) (see Appendix, Note 9).

$\mathbf{P}$ represents a vector in the direction opposite to the radius vector, *i. e.* in the direction of the acceleration, while $\mathbf{Q}$ represents a vector perpendicular thereto. $\beta\mathbf{Q}$ thus acts in (53) exactly like a current density in giving rise to a magnetic field. Moreover, it turns out that the value which has to be provided for $\frac{d\rho_+}{dt}$ in order to give rise to the necessary atmospheric electric current is such that both $d\rho_+/dt$ and $d^2\rho_+/dt^2$ are negligible as regards their power to give rise to values of P_t and Q_t which would contribute appreciably to $\phi_+ + \phi_-$ through (52), and so to $\mathbf{E}_+ + \mathbf{E}_-$ through (54) (see Appendix, Note 9).

The smallness of $\phi_+ + \phi_-$ is very important. Had we attempted to choose for $\mathbf{S}_+$, $ic(S_t)_+$ a 4-vector such as would cause a piece of moving matter to be the equivalent of a current in the general field equations in such a way that the apparent current density was proportional to the velocity of the matter, we could not have avoided the presence of a fourth component of undesirable magnitude. In fact, the four components would have been in the ratio ku_x, ku_y, ku_z, kic, so that if in the general equations (39)–(53), $\mathbf{Au}$ had survived as a numerator for $\mathbf{U}_+ + \mathbf{U}_-$ after the cancellation of the parts $\rho_+ u_+$ and $\rho_- u_-$ corresponding to the positive and negative electricity in the sphere, there would

also have survived in the numerator of the integral for $\phi_- + \phi_-$ the quantity A. The result of this would have been that we should have been compelled to admit that a rotating sphere which gave rise to a given magnetic field as a result of its rotating neutral matter would also give rise to an electric field, and this electric field would be as large as would be that electrical field which we should have had if we had obtained the magnetic field in question by the rotation of a solid sphere of electricity. There is thus a very fundamental objection to any theory which supposes that a piece of neutral matter may act to produce magnetic field entirely in virtue of its velocity.

It is not therefore to the expressions αP_t and βQ_t that we shall look for an explanation of the earth's electric field, but rather to the accumulation of unbalanced negative charge resulting from the continual death of the positive electricity. This accumulation of negative charge piles up until the field which it produces causes an atmospheric electric current into space of such amount as to maintain equilibrium with the rate of death of positive electricity.

It is by equating the atmospheric electric current to the volume integral of $\partial\rho_+/\partial t$ throughout the sphere that we shall determine the magnitude of the numerical factor in $a\mathbf{P}$; for, as will appear, div $(\beta\mathbf{Q})$ is zero for the case of uniform rotation.

If Γ_r and Γ_ψ are respectively the components of a vector in the direction of the radius vector and tangential to a circle about the origin, we have, in cylindrical coordinates for the case where there is no variation of the quantities along the z axis,

$$\mathrm{Div}\,\Gamma = \frac{1}{r}\frac{\partial}{\partial r}(r\Gamma_r) + \frac{1}{r}\frac{\partial \Gamma_\psi}{\partial \psi}. \quad . \quad . \quad . \quad (63)$$

From this, and from (61), we see that, if β is independent of ψ as it is from symmetry *,

$$\mathrm{Div}\,\beta\mathbf{Q} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

* It might be of interest to call attention to a further fact. We have seen that $a\mathbf{P}$ represents a vector in a radial direction, and $\beta\mathbf{Q}$ represents a vector in a direction tangential to a circle about the origin. The 3-vector formed from the 4-vector of next higher order is radial and opposite in direction to $a\mathbf{P}$. In fact, the 3-vectors formed from the 4-vectors of successively higher orders are at right angles to each other, each one being advanced one right angle in relation to its predecessor. It follows from this that, if we call the ordinary vector $\rho\mathbf{u}$ of electromagnetic theory the first, $a\mathbf{P}$ the second, $\beta\mathbf{Q}$ the third, and so on, then, for uniform rotation, all vectors of odd orders are such as to have no divergence and so contribute nothing to the violation of the equation of

Now it turns out that while the main terms of (51) are of the first order of magnitude in α, those involving the time derivatives of αP_t and βQ_t are of the third order in α, and are quite negligible (see Appendix, Note 9). Indeed, they would be absolutely zero except for the slight departure from a steady state resulting from the slow death of the positive electricity. Omitting, then, the terms in question and using (59) and (64), (51) becomes

$$\frac{-\partial\rho_+}{\partial t} = -\operatorname{div}\omega^2\rho_+\alpha k_+ r = -\frac{\omega^2\rho_+}{r}\frac{\partial}{\partial r}(\alpha k_+ r^5). \quad . \quad (65)$$

The form of $-\partial\rho_+/\partial t$ as a function of r and ω will depend upon the form of the invariant α. If α is taken of such form that for uniform rotation as a rigid body $k_+\alpha$ is a constant independent of r, we have, for this case

$$\frac{-\partial\rho_+}{\partial t} = -2\omega^2\rho_+\alpha k_+ \quad . \quad . \quad . \quad . \quad . \quad (66)$$

In the steady state the atmospheric electric current from the whole earth will consequently be

$$J = \frac{8\pi}{3}\omega^2\rho_+\alpha k_+ a^3. \quad . \quad . \quad . \quad . \quad . \quad (67)$$

And if the material density D is proportional to the number of protons per c.c., as is approximately true, and α is a constant, we should have J proportional to $D\omega^2a^3$ approximately. In Table I. the values of J are given for this case, the values here being in electrostatic units, and based on the known value -3×10^{12} e.s.u. for the earth. It will be seen that the small sphere would give an easily measurable current density amounting to 10^3 e.s.u. If, however, we can secure a value of J proportional to the first power of ω, so that J is proportional to $D\omega a^3$, the current for the small sphere would be practically immeasurable, and even for the sun the value suggested would not be unreasonable in comparison with the known value for the earth. As we shall see, it is possible to choose, for α, an invariant which for uniform

continuity, while those of even order do give rise to such violation. On the other hand, the vectors of odd order, being all parallel to $\rho\mathbf{u}$, act in the vector potential of (53) as the equivalents of currents flowing in circles about the axis of rotation. They are thus of a nature such as to provide in a general way for a magnetic field like that of the earth. On the other hand, the vectors of even order, being radial, are totally unsuitable for such purposes. Happily the magnitudes which it becomes necessary to assign to them are such that their influence on the magnetic field is totally negligible.

rotation reduces to

$$\alpha = \alpha_0 k^{-1} \omega^{-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

where α_0 is independent of r and ω, so that, anticipating to the extent of assuming this value for α, we have, from (67),

$$J = \frac{8\pi}{3} \alpha_0 \rho_+ \omega a^3,$$

or, if m is the combined mass of a proton and electron, e_+ the charge of a proton, and D the density of the earth,

$$J = \frac{8\pi}{3} \alpha_0 \frac{e_+}{m} D \omega a^3. \quad . \quad . \quad . \quad . \quad (69)$$

The atmospheric electric current from the whole earth amounts to about -3×10^{12} e.s.u., so that, putting

$$a = 6{\cdot}4 \times 10^8 \text{ cm.}, \ \omega = 7{\cdot}3 \times 10^{-5}, \ D = 5{\cdot}5,$$
$$e_+ = 4{\cdot}8 \times 10^{-19} \text{ e.s.u.}, \ m = 1{\cdot}64 \times 10^{-24},$$

we find

$$\alpha_0 = -1{\cdot}2 \times 10^{-26}. \quad . \quad . \quad . \quad . \quad . \quad (70)$$

From (66) and (68)

$$-\frac{1}{\rho_+} \frac{d\rho_+}{dt} = -2\omega\alpha_0,$$

so that

$$-\frac{1}{\rho_+} \frac{\partial \rho_+}{\partial t} = 1{\cdot}7 \times 10^{-30},$$

which corresponds to a loss of charge amounting to less than 1 proton per c.c. per day. The required rate of death would correspond to a loss of 0·5 per cent. of the earth's mass in 10^{20} years.

Using in (68) the value of α_0 given in (70) and referring to (53), we readily find that, quite apart from the fact that the vector $\alpha\mathbf{P}$ is in a direction perpendicular to that necessary to give the earth's magnetic field, its magnitude is quite negligible as regards any measurable influence it may have on $\mathbf{U}_+ + \mathbf{U}_-$ (see Appendix, Note 10). It is thus to the term $\beta\mathbf{Q}$ in (53) that we must look for the origin of the magnetic field. As we have already remarked, this term is a vector in the proper direction, and it is, in fact, the analytical equivalent of a tangential current density of amount $\beta\mathbf{Q}$, since it occurs in the vector potential exactly in the way that such a current density would occur. Putting i for this apparent current density, we thus have

$$\mathbf{i} = \beta\mathbf{Q}$$

or, from (61),

$$i = -\beta\rho_+ k_+^2 r \omega^3, \quad . \quad . \quad . \quad . \quad . \quad (71)$$

the minus sign indicating that β must be negative if i is to correspond in sign to ω.

Now we have seen that, in order to conform to the relative requirements of the sun, the earth, and the small sphere of high angular velocity, it is necessary to have i proportional to $Dr^3\omega^4$. Hence the invariant β must be such that, for uniform rotation, it reduces to

$$\beta_0 r^2\omega/k_+^2,$$

where β_0 is independent of r and ω. However, the factor k_+ is so nearly equal to unity that its presence or absence does not appreciably affect the conclusions.

Choice of the Invariants α and β.

As we have already seen, it is necessary to choose for α and β invariants which, for a case of uniform rotation, reduce to $\alpha_0 k_+^{-1}\omega^{-1}$ and $\beta_0 r^2\omega/k_+^2$ respectively, where α_0 and β_0 are independent of r and ω.

The simplest way to form invariants which are not mere constants is to take the scalar product of two 4-vectors. The 4-vectors naturally at our disposal for this purpose are the velocity 4-vector, and all the 4-vectors of higher order obtained by operating successively with $k_+\frac{d}{dt}$.

Table II. gives the components of these 4-vectors, T_1, T_2, T_3, etc., referring symbolically to the whole 4-vector, and $\frac{d}{ds}$ being written for the operator $k_+\frac{d}{dt}$. The last two columns give the form to which the 4-vector degenerates for a case of uniform rotation. The first of these two columns gives the resultant 3-vector formed by the first three components of the corresponding 4-vector, and the direction of the 3-vector is indicated by the arrow attached to the circle. It will be observed that the three vectors corresponding to T_1, T_2, T_3, ... etc., are advanced successively in direction by one right angle.

These degenerate forms are obtained immediately if we remember that for uniform rotation $\frac{dk_+}{dt}$ is zero. We can readily see from the directions of the 3-vectors and from the fact that all the fourth components are zero except the first, that any scalar product of a 4-vector of odd order with one of even order is zero. Only scalar products of odd or of even

4-vectors survive, and these are obtained immediately in degenerate form by multiplying together the corresponding quantities in the column next to the last.

TABLE II.

4-vector.	Components.				Degenerate Forms.	
	x.	y.	z.	4th.	Resultant 3-vector.	4th component.
T_1	k_+u_x	k_+u_y	k_+u_z	k_+ic	$k_+r\omega$	kic
T_2	$\frac{d}{ds}(k_+u_x)$	$\frac{d}{ds}(k_+u_y)$	$\frac{d}{ds}(k_+u_z)$	$\frac{d}{ds}(k_+ic)$	$k_+{}^2r\omega^2$	0
T_3	$\frac{d^2}{ds^2}(k_+u_x)$	$\frac{d^2}{ds^2}(k_+u_y)$	$\frac{d^2}{ds^2}(k_+u_z)$	$\frac{d^2}{ds^2}(k_+ic)$	$k_+{}^3r\omega^3$	0
T_4	$\frac{d^3}{ds^3}(k_+u_x)$	$\frac{d^3}{ds^3}(k_+u_y)$	$\frac{d^3}{ds^3}(k_+u_z)$	$\frac{d^3}{ds^3}(k_+ic)$	$k_+ r\omega^4$	0
T_5	etc.	etc.	etc.	etc.	$k_+{}^5r\omega^5$	0

There are several ways in which we may build up invariants which degenerate to the desired forms $\alpha_0 k_+{}^{-1}\omega^{-1}$ and $\beta_0 r^2\omega/k_+{}^2$. Thus, for example,

$$\frac{(T_1 \cdot T_3)^{1/4}}{(T_3 \cdot T_5)^{1/4}} \text{ degenerates to } k_+{}^{-1}\omega^{-1},$$

and

$$\frac{(T_1 \cdot T_3)^{7/4}}{(T_3 \cdot T_5)^{3/4}} \text{ degenerates to } k_+ r^2\omega,$$

where the parenthesis with the dot denotes the scalar product of the two 4-vectors designated by the corresponding T's. The factor k_+ in the last expression in place of $k_+{}^{-2}$ causes no trouble since it is very nearly equal to unity, and therefore does not affect the functional form of β appreciably. Thus

two of many forms which serve our purpose for α and β are

$$\alpha=\alpha_0\frac{(T_1\,.\,T_3)^{1.4}}{(T_3\,.\,T_5)^{1/4}}, \quad . \quad . \quad . \quad . \quad . \quad (72)$$

$$\beta=\beta_0\frac{(T_1\,.\,T_3)^{7/4}}{(T_3\,.\,T_5)^{3/4}}. \quad . \quad . \quad . \quad . \quad . \quad (73)$$

With this form of β our apparent current density is

$$i=-\beta_0\rho_+k_+^3\omega^4r^3,$$

or, if m is the combined mass of a proton and an electron, e_+ the charge on a proton, and D the density of the substance of the earth,

$$i=\beta_0\frac{e_+\mathrm{D}}{m}k_+^3\omega^4r^3.$$

From (87), in Appendix, Note 1, we consequently have, for the magnetic field at the north pole,

$$-\frac{64\pi}{315}\beta_0\frac{e_+\mathrm{D}}{cm}k_+^3\omega^4a^4,$$

where the negative sign indicates for a positive β_0 a field directed radially inwards for a rotation from west to east. k_+ is sensibly unity; so that, putting $\mathrm{H}=0{\cdot}5$ c.g.s. unit at the pole, $e_+/m=2{\cdot}9\times10^{14}$, $\mathrm{D}=5{\cdot}5$, $\omega=7{\cdot}3\times10^{-5}$, and $a=6{\cdot}4\times10^8$ cm., we find

$$\beta_0=3{\cdot}1\times10^{-24}. \quad . \quad . \quad . \quad . \quad . \quad (74)$$

We have thus determined forms of $\mathbf{P}$ and $\mathbf{Q}$ and of α and β which will make equations (25)–(34) give rise to a magnetic field comparable with that of the earth and to an atmospheric electric current, and so to a potential gradient comparable with that of the earth. Moreover, the forms of our expressions are such as to be consistent with the requirements imposed by the sun and by a small sphere rotating at high speed, and they are consistent with restricted relativity.

Gravitation.

The incorporation of gravitation in the scheme comes about essentially along the lines of the theory of Lorentz.

In the first place we shall regard the right-hand side of (33) and (34) when multiplied by e as representing respectively the force on a proton and electron to the extent of believing that if we evaluate the total force due to one piece

of neutral matter on another by adding up the forces (as above understood) on the individual protons and electrons, the result will represent the gravitational force between the pieces of matter. If we discuss the case for matter at rest we can neglect the terms involving velocity and magnetic field. As a matter of fact, it is easy to see that these terms are negligible even when the matter is in motion, as are also those correcting terms on the *fields* brought about by the modifications we have introduced into the electrodynamic laws (see Appendix, Note 11). Thus, confining ourselves to the values of $\mathbf{E}_+$ and $\mathbf{E}_-$ calculated for stationary matter, and using ordinary electrostatic units, we have, for the forces δF_+ and δF_- on a proton and electron respectively, and due to an element of matter of volume $d\tau_1$ containing N_1 protons and N_1 electrons,

$$\delta F_+ = \delta F_- = \frac{N_1 e^2 (1-\lambda)}{R^2} d\tau_1 ;$$

so that the total force on an element of matter of volume $d\tau_2$ containing N_2 protons and electrons per c.c. is

$$\delta F = \frac{2 N_1 N_2 (1-\lambda) e^2}{R^2} d\tau_1 d\tau_2 .$$

If m refers to the sum of the masses of a proton and electron, and if D_1 and D_2 are the densities of the substances

$$\delta F = 2 D_1 D_2 \left(\frac{e}{m}\right)^2 (1-\lambda)\, d\tau_1 d\tau_2 .$$

This must be equated to

$$-\frac{G D_1 D_2}{R^2} d\tau_1 d\tau_2 ,$$

where G is the gravitational constant.

Hence

$$\lambda - 1 = \frac{G}{2}\left(\frac{m}{e}\right)^2 . \quad . \quad . \quad . \quad . \quad . \quad (75)$$

Putting

$$G = 6{\cdot}6 \times 10^{-8}, \quad \frac{\rho}{m} = 2{\cdot}9 \times 10^{14},$$

we have

$$\lambda = 1 + 3{\cdot}9 \times 10^{-37} . \quad . \quad . \quad . \quad . \quad . \quad (76)$$

Summary.

Collecting our results from equations (23)–(32) for the field equations, from (33) and (34) for the force equations,

from (55)–(58) for the forms of $\mathbf{P}$, P_t, $\mathbf{Q}$, Q_t, and from (72) and (73) and Table II. for α and β, we have as follows :—

$$\frac{1}{c}\left\{\rho_+\mathbf{u}_+ + \alpha_0\frac{(T_1\,.\,T_3)^{1/4}}{(T_3\,.\,T_5)^{1/4}}k_+\frac{d}{dt}(\rho_+\mathbf{u}_+)\right.$$
$$\left.+\beta_0\frac{(T_1\,.\,T_3)^{7/4}}{(T_3\,.\,T_5)^{3/4}}k_+\frac{d}{dt}k_+\frac{d}{dt}(\rho_+\mathbf{u}_+)+\frac{\partial\mathbf{E}_+}{\partial t}\right\}=\text{curl}\,\mathbf{H}_+, \quad (77)$$

$$\rho_+ + \alpha_0\frac{(T_1\,.\,T_3)^{1/4}}{(T_3\,.\,T_5)^{1/4}}k_+\frac{d\rho_+}{dt}$$
$$+\beta_0\frac{(T_1\,.\,T_3)^{7/4}}{(T_3\,.\,T_5)^{3/4}}k_+\frac{d}{dt}k_+\frac{d\rho_+}{dt}=\text{div}\,\mathbf{E}_+, \quad (78)$$

$$-\frac{1}{c}\frac{\partial\mathbf{H}_+}{\partial t}=\text{curl}\,\mathbf{E}_+, \quad . \quad . \quad . \quad (79)$$

$$0=\text{div}\,\mathbf{H}_+, \quad . \quad . \quad . \quad (80)$$

$$\frac{1}{c}\left(\rho_-\mathbf{u}_- + \frac{\partial\mathbf{E}_-}{\partial t}\right)=\text{curl}\,\mathbf{H}_-, \quad . \quad . \quad . \quad (81)$$

$$\rho_-=\text{div}\,\mathbf{E}_-, \quad . \quad . \quad . \quad (82)$$

$$-\frac{1}{c}\frac{\partial\mathbf{H}_-}{\partial t}=\text{curl}\,\mathbf{E}_-, \quad . \quad . \quad . \quad (83)$$

$$0=\text{div}\,\mathbf{H}_-, \quad . \quad . \quad . \quad (84)$$

$$\frac{m_+}{e_+}\frac{d}{dt}(k_+\mathbf{w}_+)=\mathbf{E}_+ + \frac{[\mathbf{w}_+\mathbf{H}_+]}{c}+\lambda\left(\mathbf{E}_- + \frac{[\mathbf{w}_+\mathbf{H}_-]}{c}\right), \quad (85)$$

$$\frac{m_-}{e}\frac{d}{dt}(k_-\mathbf{w}_-)=\mathbf{E}_- + \frac{[\mathbf{w}_-\mathbf{H}_-]}{c}+\lambda\left(\mathbf{E}_+ + \frac{[\mathbf{w}_-\mathbf{H}_+]}{c}\right), \quad (86)$$

where the meanings of the T's are given in Table II., and the value of λ by (75).

These equations are invariant under the transformation of the restricted theory of relativity, and they can readily be generalized to a form invariant in the sense of the general theory of relativity. With the values

$$\alpha_0=-1{\cdot}2\times10^{-26}, \quad \beta_0=3{\cdot}1\times10^{-24}, \quad \lambda=1+3{\cdot}9\times10^{-37},$$

as given by equations (70), (74), and (76), they predict, for a sphere of the earth's size rotating with the earth's angular velocity, a magnetic field comparable with the earth's field but symmetrical about the axis of rotation. They give a death of positive electricity amounting to a disappearance of 0·5 per cent. of the earth's mass in 10^{20} years, leaving a surplus of negative electricity which passes off as an atmospheric electric current equal in

magnitude to the earth's atmospheric electric current and corresponding, therefore, to a potential gradient equal to the earth's potential gradient. Moreover, the value which they predict for the magnetic field of the sun is correct within the limits of our knowledge of that magnitude, and the value which they predict for the sun's atmospheric electric current is not unreasonable, although we have no data to test it. They predict for a small sphere 10 cm. in radius and of the earth's density, rotating 100 times per second, a magnetic field and a rate of accumulation of surplus negative electricity practically immeasurable under the possible conditions of experimentation. They predict an attraction between neutral matter to the proper extent determined by the gravitational constant.

The generalization which we have made in the electrodynamic equations is only one of many which may be made for the above purposes. Thus, as we have seen, the two additional terms in (77) and in (78) might be extended into a series involving higher time derivatives of the velocity, and the invariants involving the T's might be chosen in various ways; again, the left-hand sides of (85) and (86) might be extended into series involving higher time derivatives of the velocity.

It is important to observe that, although the additional terms have been chosen by an appeal to the forms to which they degenerate for uniform rotation, the equations in the form presented in (77)–(86) or their further generalizations along lines indicated above are to be regarded as applicable to any kind of motion. It may be added that our reason for throwing the onus of the generalization on the positive electricity rather than the negative, or both, is that we have wished to avoid the discussion of such difficult questions as might arise in the matter of the conservation of charge in the case of rapid changes of velocity of β-rays of very high speed. Even the question of conservation of charge to the extent required by experience in the case of such changes of speed as are suffered by α-particles is one which invokes further discussion, but is too large a subject to enter into here. However, it will readily be seen that we have at our disposal plenty of latitude for avoiding such difficulties. Thus, to take a hypothetical case involving, for simplicity, only uniform rotation, suppose that we should encounter in the atom a situation of this kind involving rotation with very high angular velocity. It is possible that expression (66), with α as given by (68), and with the value of α_0 given by (70), would lead to a rate of death of charge

inconsistent with the facts. However, it is quite possible to replace the invariant α as given by (72) and which degenerates to (68) by, for example,

$$\alpha=\alpha_0\frac{(T_1\,.\,T_3)^{1/4}}{(T_3\,.\,T_5)^{1/4}}\left\{1+\gamma\frac{(T_3\,.\,T_5)^{s/4}}{(T_1\,.\,T_3)^{s/4}}\right\}^{-1},$$

where γ is a very small constant, and s is a positive integer. For uniform rotation α will now degenerate to

$$\alpha=\alpha_0 k_+^{-1}\omega^{-1}\{1+\gamma k_+^{\,s}\omega^s\}^{-1}.$$

By choosing a suitably large value of s and a suitably small value of γ, we can make $\gamma k_+^{\,s}\omega^s$ insignificant for angular velocities comparable with that of the earth's rotation, or even with that of a sphere rotating with any practicable speed attainable with bodies of laboratory dimensions; and yet we can arrange that the term is as large as we choose for the high angular velocities concerned in the atomic problem. For very high angular velocities α will thus become

$$\alpha=\alpha_0 k_+^{-1}\omega^{-1}/\gamma k_+^{\,s}\omega^s,$$

and (66) will become

$$-\frac{1}{\rho_+}\frac{\partial\rho_+}{\partial t}=-\frac{2\omega\alpha_0}{\gamma k_+^{\,s}\omega^s},$$

which on account of the large value of the denominator for very large values of ω will result in very small values of $\frac{1}{\rho_+}\frac{\partial\rho_+}{\partial t}$ for such cases.

Another question related to this matter arises even in the slow rates of death of charge involved in the earth's rotation. Are we to assume that the death takes place uniformly with time in each proton? A more reasonable view would be to the effect that only occasionally is a proton affected and then the whole proton dies. On such a view it would be necessary to appeal to the same sort of arguments as are made in attempts to reconcile quantum phenomena with classical electrodynamics, and regard equations (77)–(86) as holding only in a statistical sense.

The Reasonableness of the Equations.

From a purely mathematical standpoint such a generalization as we have made is satisfying in that it replaces the term $\rho\mathbf{u}$ of classical electrodynamics by an infinite series containing all orders of time derivatives of the velocities.

If one asks what the physical significance of these extra terms is, we can well reply that they have as much right to physical significance as the term $\rho\mathbf{u}$, and only lack of familiarity with them suggests otherwise. If, however, one is pressed for a statement which will be more agreeable to the non-mathematical mind, one may speak thus :—

Suppose we have a circle of wire carrying a current. Then, according to ordinary physical ideas, we imagine the magnetic field as produced entirely by the velocity and density of the electricity. However, the electricity has acceleration $\omega^2 r$, rate of change of acceleration, and so on. Why should it not be the case that, even for a steady state *, where $\mathbf{E}$ and $\mathbf{H}$ are independent of the time, the acceleration, rate of change of acceleration, etc., give rise to magnetic fields? If such were true, then, in the case of a current flowing in a circle, for example, we should get from that current, when produced by a density ρ and a velocity $\mathbf{u}$, a different magnetic field from that produced by a density $0{\cdot}5\,\rho$ and a velocity $2\mathbf{u}$. It is such a state of affairs as this that the extra terms in our equations provide for ; and, if the phenomena which they represent were of sufficiently large magnitude to impress themselves upon us in everyday experiments, we should doubtless learn to attach as strong a physical significance to these terms as we now attach to the main term $\rho\mathbf{u}$.

Of course the actual values of the terms in our equations are extremely small when applied to such motions as are concerned in the earth's rotation. Thus, for this case, the two additional terms in (77) amount at most to only one part in 10^{26} and five parts in 10^{19} respectively, in comparison with the term $\rho\mathbf{u}_4$; and, as we have seen, the quantity λ in (85) and (86) differs from unity by only $3{\cdot}9\times10^{-37}$.

The question of whether the foregoing ideas do constitute the germ of an explanation of terrestrial magnetism and atmospheric electric phenomena is one which is perhaps apart from their merits as forming a consistent scheme in themselves. It is not without interest to observe, however, that if anyone objects to them as constituting a theory of the phenomena in question, he may at least take the facts that the earth's magnetic field and atmospheric-electric current are as small as they are as evidence of an extraordinary completeness in the symmetry of the equations for

* We here limit the discussion to that for a steady state, as, in other cases, even the classical electrodynamics causes the magnetic field to depend upon the accelerations and higher derivatives.

the fields due to positive and negative electricity, particularly as regards any generalization of those equations along the lines we have indicated.

Appendix.

Note 1.—Let there be a circular ring carrying a current I e.s.u., the ring being of such size that its diameter subtends an angle 2β at the centre of a sphere of radius σ. Then the magnetic potential Ω at a point R, θ outside the sphere is *, in e.m.u.,

$$\Omega=\frac{2\pi \mathrm{I}}{c}\sin^2\beta\sum_{s=1}^{s=\infty}\left(\frac{1}{s+1}\right)\frac{\sigma^{s+1}}{\mathrm{R}^{s+1}}\frac{d\mathrm{P}_s(\beta)}{d\mu}\mathrm{P}_s(\theta),$$

where $\mu=\cos\beta$, and the P's are the Legendre coefficients.

Apply this to a ring of cross-section $\sigma d\beta d\sigma$ carrying a current of density

$$i=\mathrm{AD}\omega^m r^n=\mathrm{AD}\omega^m\sigma^n\sin^n\beta,$$

as specified in the text. Integrate from $\beta=$ zero to π and from $\sigma=$ zero to a. Then form minus the differential coefficient with respect to R and put $\mathrm{R}=a$, to obtain the vertical component of the field at the surface.

In this way we obtain

$$\mathrm{H}_z=\frac{2\pi}{c}\mathrm{AD}\omega^m a^{n+1}(n+1)\sum_{s=1}^{s=\infty}\frac{\mathrm{P}_s(\theta)}{n+s+3}\int_{-1}^{+1}(1-\mu^2)^{\frac{n-1}{2}}\mu\mathrm{P}_s(\beta)d\mu.$$

For $\theta=0$ the quantity under the sum becomes a function of n only, so that

$$\mathrm{H}_z=\mathrm{AD}\omega^m a^{n+1}\mathrm{F}(n).$$

Working out, in greater detail, the result for $n=3$, we readily find

$$\mathrm{H}_z=\frac{32}{35c}\mathrm{A}\pi\mathrm{D}\omega^m a^4\left[\frac{\mathrm{P}_1(\theta)}{3}-\frac{\mathrm{P}_3(\theta)}{9}\right].$$

And, for $\theta=0$, *i. e.* at the pole,

$$\mathrm{H}_z=\frac{64}{315c}\mathrm{A}\pi\mathrm{D}\omega^m a^4. \quad . \quad . \quad . \quad . \quad (87)$$

Note 2.—This equation makes its appearance in electrodynamics through the assumption that the electron moves so that the integral of $\left(\mathbf{E}+\frac{[\mathbf{uH}]}{c}\right)\rho d\tau$ taken all over the electron is zero, $\mathbf{E}$ and $\mathbf{H}$ here referring to the resulting field, including the field of the electron itself. It is by

* Maxwell's 'Treatise on Electricity and Magnetism,' 3rd edition, vol. ii. p. 333.

separating this integral into two parts, one due to the field of the electron and the other to the external field, and then evaluating the former in terms of the motion of the electron that the terms on the right-hand side of (6) find their origin, and with them the significance of electronic mass in relation to the charge and electronic radius. An assumption has to be made as to the variation of the shape of the electron with its motion. It seems to have been customary to assume that at each instant the electron suffers the Lorentzian contraction appropriate to a steady velocity equal to the velocity at that instant. Under these conditions the law of motion derived is not invariant under the Lorentzian transformation, as was shown by S. Jacobsohn *.

Moreover, such an assumption as to change of shape with velocity would, in certain cases, lead to the conclusion that parts of the electron would have to travel with a velocity greater than that of light. For example, when the acceleration is so great that, starting from rest, the centre of the electron attains the velocity c in a time a/c, where a is the radius of the spherical electron at rest, the assumption would cause the rear parts of the electron to attain a velocity greater than c, in order that the postulated contraction could be assumed.

The equation of motion of an electron has been expressed in a modified form by Leigh Page †, who assumes that, at each instant, the electron is a sphere with all of its parts moving with equal though not constant velocity when it is referred to a system of axes with respect to which it is momentarily at rest, and that in this system of axes its acceleration and higher derivatives are such as to give zero for the integral of $\left(\mathbf{E}+\frac{[\mathbf{uH}]}{c}\right)\rho\, d\tau$ when evaluated over it.

When this law is expressed in terms of an arbitrary system of axes, it assumes the form

$$\iiint\left(\mathbf{E}+\frac{[\mathbf{uH}]}{c}\right)\rho\, d\tau=\frac{e^2}{6\pi ac^2}\frac{d}{dt}\mathbf{w}\left(1-\frac{q^2}{c^2}\right)^{-\frac{1}{2}}+\mathbf{B},$$

where $\mathbf{B}$ involves all the time derivatives of the motion, and where $\mathbf{E}$ and $\mathbf{H}$ now refer to the external field, and $\mathbf{w}$ refers to the velocity of the centre of the electron. If one

* In a paper entitled "Note on the Force Equation of Electrodynamics," read before the American Mathematical Congress, Toronto, August 1924.

† Phys. Rev. vol. xi. p. 398 (1918).

assumes that $\mathbf{E}$ and $\mathbf{H}$ in this equation are sensibly constant over the electron, the left-hand side of the equation assumes the form $\left(\mathbf{E}+\frac{[\mathbf{wH}]}{c}\right)e$; and the equation so obtained is invariant*. However, it would seem that the invariance does not hold to a degree of approximation which takes account of the variation of the external field over the electron, a condition which is not out of the realms of practical interest when one considers the sharp changes of field which an electron may encounter when coming into the vicinity of another which is moving with a velocity comparable with c, and whose tubes of force are therefore concentrated greatly towards its equatorial plane.

It would thus seem that the assumption of zero force on the electron does not lead, in any of its forms, to expressions which are well adapted formally to the requirements of relativity. However, it is possible to write down an equation which has all the generality of those suggested by electrodynamics and more by equating $k\left(\mathbf{E}+\frac{[\mathbf{wH}]}{c}\right)e$ to a series composed of the vectors formed from the first three components of the acceleration 4-vector, and the first three components of all the 4-vectors of higher order, each vector being provided with an invariant coefficient, the understanding being that $\mathbf{E}$ and $\mathbf{H}$ refer to the external field at a specified point in the electron, and $k=\left(1-\frac{q^2}{c^2}\right)^{-\frac{1}{2}}$. The generalization may be further enhanced by the insertion of invariants under any of the time derivatives, a procedure which does not destroy the 4-vector character. It is known that the three components of $k\left(\mathbf{E}+\frac{[\mathbf{wH}]}{c}\right)$, together with $ki(\mathbf{E}\,.\,\mathbf{w})/c$, constitute a 4-vector, i being $\sqrt{-1}$. Thus the equation obtained will be invariant, provided that the invariant coefficients are such that the 4-vector composed of the series of terms referred to possesses the property that its fourth component is i/c times the scalar product of $\mathbf{w}$ with its other three components (see Appendix, Note 6). The series of 4-vectors contains derivatives of all orders so that it has all the desired characteristics for exhibiting radiation reactions and the like, and its first and most important term is, for the case where the invariants associated with it are constants, identical in form with the corresponding

* L. Page, Phys. Rev. vol. xxiv. pp. 627–630 (1924).

term in the ordinary electrodynamic equation. Its generality is, however, enhanced in comparison with the electrodynamic expression by the greater arbitrariness of the invariants associated with the various 4-vectors. It is in such an extended sense as this that we shall understand equation (6) and equations (33) and (34) for the most general case.

Note 3.—Equation (16) is automatically satisfied by (19). Substituting from (19) in (15), we find that the latter equation is satisfied if

$$\operatorname{curl}\left(\mathbf{E}+\frac{1}{c}\frac{\partial \mathbf{U}}{\partial t}\right)=0,$$

and this is satisfied by (18).

Substituting from (18) and (19) in (13), we find that (13) is satisfied if

$$\frac{\mathbf{S}}{c}=\frac{1}{c^2}\frac{\partial^2 \mathbf{U}}{\partial t^2}+\frac{1}{c}\operatorname{grad}\frac{\partial \phi}{\partial t}+\operatorname{curl}\operatorname{curl}\mathbf{U};$$

i. e., if

$$-\frac{\mathbf{S}}{c}=\nabla^2\mathbf{U}-\frac{1}{c^2}\frac{\partial^2 \mathbf{U}}{\partial t^2}-\operatorname{grad}\left\{\operatorname{div}\mathbf{U}+\frac{1}{c}\frac{\partial \phi}{\partial t}\right\},$$

and this is satisfied if (21) is true.

Again, substituting from (18) in (14), we find the latter satisfied if

$$S_t=-\frac{1}{c}\frac{\partial}{\partial t}\operatorname{div}\mathbf{U}-\nabla^2\phi;$$

i. e., if

$$-\frac{S_t}{c}=\nabla^2\phi-\frac{1}{c^2}\frac{\partial^2\phi}{\partial t^2}+\frac{1}{c}\frac{\partial}{\partial t}\left\{\operatorname{div}\mathbf{U}+\frac{1}{c}\frac{\partial \phi}{\partial t}\right\},$$

which, again, is true if (21) holds. Hence (13)–(16), which also imply (17), are satisfied by the solutions (18)–(21).

Note 4.—Consider the second of equations (20). Divide all space into volume elements $d\tau$. The value $\mathbf{U}_\lambda$ of $\mathbf{U}$ corresponding to an element of length $d\lambda$ at any point P at time t is determined by the values of $\mathbf{S}_\lambda$ in the various volume elements estimated at times $t-\mathrm{R}/c$, where R is the radius vector from P to the corresponding volume element. Now consider a point P′ displaced an infinitesimal amount $d\lambda$ from P, and again divide all space into volume elements $d\tau'$ such that each of them may be regarded as

obtained from a corresponding volume element $d\tau$ by displacement equal and parallel to $d\lambda$. The value of $\mathbf{U}_\lambda$ at P′ at time t is determined by the values of $\mathbf{S}_\lambda$ in the volume elements $d\tau'$ at the times R/c earlier. Thus, corresponding to the same time t at P and P′, the *effective* times in *corresponding* volume elements are the same and the distances of corresponding volume elements from P and P′ respectively are equal, so that

$$4\pi c\,(\mathbf{U}_{\lambda P'} - \mathbf{U}_{\lambda P}) = d\lambda \iiint \left[\frac{\partial \mathbf{S}_\lambda}{\partial \lambda}\right]_{\mathrm{R}} d\tau\,;$$

i. e.,

$$4\pi c \frac{\partial \mathbf{U}_\lambda}{\partial \lambda} = \iiint \left[\frac{\partial \mathbf{S}_\lambda}{\partial \lambda}\right]_{\mathrm{R}} d\tau,$$

where the square bracket has the same significance as before. By considering displacements $d\mu$, $d\nu$, perpendicular to $d\lambda$, we thus immediately derive

$$4\pi c \operatorname{div} \mathbf{U} = \iiint \frac{[\operatorname{div} \mathbf{S}]}{\mathrm{R}} d\tau. \quad . \quad . \quad . \quad (88)$$

Turning now to the first of equations (20), it is obvious that

$$4\pi \frac{\partial \phi}{\partial t} = \iiint \left[\frac{\partial S_t}{\partial t}\right]_{\mathrm{R}} d\tau, \quad . \quad . \quad . \quad . \quad (89)$$

where again the square bracket has the same significance as before ; for the effective volume elements are the same at t as at $t + dt$ for a fixed point P, and the values of S_t which are effective at times t and $t + dt$ at P are those to be found at $t - \mathrm{R}/c$ and $t + dt - \mathrm{R}/c$ in the volume element corresponding to R.

Since in every volume element at *all instants*

$$\operatorname{div} \mathbf{S} + \frac{\partial S_t}{\partial t} = 0,$$

we have, from (88) and (89),

$$\operatorname{div} \mathbf{U} = -\frac{1}{c}\frac{\partial \phi}{\partial t},$$

showing that this equation is the analytical equivalent of (17).

Note 5.—On transforming equations (2)–(5) to the system whose coordinates x', y', z', t' are specified by (22), they

revert to the same form in dashed letters, with the understanding that

$$\mathrm{E}_x' = \mathrm{E}_x, \quad \mathrm{E}_y' = \epsilon\left(\mathrm{E}_y - \frac{v}{c}\mathrm{H}_z\right), \quad \mathrm{E}_z' = \epsilon\left(\mathrm{E}_z + \frac{v}{c}\mathrm{H}_y\right), \quad (90)$$

$$\mathrm{H}_x' = \mathrm{H}_x, \quad \mathrm{H}_y' = \epsilon\left(\mathrm{H}_y + \frac{v}{c}\mathrm{E}_z\right), \quad \mathrm{H}_z' = \epsilon\left(\mathrm{H}_z - \frac{v}{c}\mathrm{E}_y\right), \quad (91)$$

$$\rho' = \epsilon\rho\left(1 - \frac{u_x v}{c^2}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (92)$$

Moreover, if $d\tau$ and $d\tau'$ are corresponding elements of volumes,

$$\rho' d\tau' = \rho\, d\tau,$$

so that the densities ρ and ρ' have corresponding significances to observers who agree on the equality of total charges in corresponding volume elements. It remains to show, however, that $\mathbf{E}'$, $\mathbf{H}'$ and $\mathbf{E}$, $\mathbf{H}$ have corresponding significances for corresponding observers. To test this point it is necessary to appeal to the definitions of $\mathbf{E}$ and $\mathbf{H}$. It would seem that the customary treatments of the matter leave much to be desired. This will immediately be apparent to anyone who takes as his definition for $\mathbf{H}$ the force on unit pole, and tries to convince himself that $\mathbf{H}'$ is the corresponding quantity which the observer in the dashed system would measure for the force on a unit pole. As a matter of fact, the whole significance of the invariance is best exhibited by a line of reasoning which does not invoke any definitions of $\mathbf{E}$ and $\mathbf{H}$ in terms of the force on anything; for at best such a procedure becomes meaningless when applied to the field at a *point inside* an electron, for example, in which case it is impossible to fall back upon the approximation that the field is sensibly constant over the entity which is used to measure it. We shall first outline the procedure in terms of the more logical attitude.

Significance of the invariance apart from definition of the fields in terms of forces on assigned entities.

In the cases of the classical equations (2)–(6) the starting-point is the assumption of an invariant (the charge) associated with any element of volume. The density ρ is defined as the value of the invariant divided by the volume element. This leads to the law of transformation (92). Equations (7)–(11) or their analytical equivalents (2)–(5) now constitute the *definitions* of $\mathbf{E}$ and $\mathbf{H}$. Since equations (2)–(5)

revert to the same form on transformation with $\mathbf{E}'$, $\mathbf{H}'$ as defined by (90) and (91) replacing $\mathbf{E}$ and $\mathbf{H}$, with ρ' given by (92), and with $\mathbf{u}'$ as given by the Lorentzian transformation replacing $\mathbf{u}$, their solutions (7)–(11) also revert to corresponding forms with ρ' as defined by (92). Since, however, with ρ' defined by (92) the equations insure the invariance of $\rho d\tau$, it follows that the ρ' defined by (92) is the quantity obtained by dividing the primary invariant (the charge in a volume element) by the volume element. Thus, in terms of the original invariant, ρ', $\mathbf{E}'$, and $\mathbf{H}'$ and ρ, $\mathbf{E}$, $\mathbf{H}$ have corresponding significances to corresponding observers. So far there has been no statement of law—all has been the erection of scaffolding. The law of physics now enters when we state such a relation as (6) as holding between the motion of an electron and the quantities $\mathbf{E}$ and $\mathbf{H}$ as above defined. The definitions of $\mathbf{E}$ and $\mathbf{H}$ have provided for $\mathbf{H}$, $-i\mathbf{E}$, transforming as a 6-vector so that, writing

$$k \equiv (1-q^2/c^2)^{-\frac{1}{2}},$$

we have, as is well known, that

$$k\left(\mathbf{E}+\frac{[\mathbf{wH}]}{c}\right), \quad ki(\mathbf{E}\,.\,\mathbf{w})/c$$

constitute a 4-vector. Consequently, if k times the right-hand side of (6) together with the scalar product of this right-hand side with iw/c forms a 4-vector, the relation (6) will be invariant (see Appendix, Note 6).

The whole law of physics implied in the scheme of equations is then to the effect that it is possible to assign to the volume elements of space numbers (the charges) which are the same for both observers and other numbers $\mathbf{u}$ which transform between the observers as a velocity transforms, and such that with the definition of ρ, $\mathbf{E}$, and $\mathbf{H}$ we have made, in terms of these two sets of numbers, equation (6) holds for the motion of an electron.

The argument proceeds in similar manner in the case of the general equations (23)–(35). Here, again, we have for the positive electricity an invariant, the positive charge in the volume element. In terms of it we define ρ_+ by dividing by the volume element. $\mathbf{P}$, $ic\mathrm{P}_t$ and $\mathbf{Q}$, $ic\mathrm{Q}_t$ then become defined in such manner as we have adopted in equations (55)–(58) for example, and the invariants α and β become constructed out of such quantities as have already been defined. If α, β, $\mathbf{P}$, P_t, $\mathbf{Q}$, Q_t are to have in their expressions anything other than the quantities already

defined or quantities which can be constructed from them, it will be necessary to make explicit definitions of these quantities in senses which would have meanings for the two observers. Presumably this would be done by defining them in terms of certain invariants as ρ_+ is defined in terms of the invariant charge in the volume element *.

$\mathbf{E}_+$, $\mathbf{H}_+$ now become defined by (25)–(28), or by their analytical equivalents of the form (18)–(20) as applied to this case. Equations (29)–(32) being of the classical form, $\mathbf{E}_-$ and $\mathbf{H}_-$ become defined as in the classical case. The foregoing definitions ensure that $\mathbf{H}_+$, $-i\mathbf{E}_+$ and $\mathbf{H}_-$, $-i\mathbf{E}_-$ transform as six vectors, and so the invariance of (33) and (34) is ensured even, if necessary, in a more general form, provided always that, if $\mathbf{W}$ is the left-hand side of one of these equations, the quantities $k\mathbf{W}$, $ik(\mathbf{W}.\mathbf{w})/c$ constitute a 4-vector. This condition is satisfied by equations (33) and (34) as they stand (see Appendix, Note 6).

Significance of the invariance when the fields are defined in terms of the forces on assigned entities.

For one who wishes to retain the concept of the field as the force on an assigned entity, the argument regarding the invariance may assume the following form.

Suppose that $k\mathbf{W}$, $ki(\mathbf{W}.\mathbf{w})/c$ constitute 4 components of a 4-vector involving time derivatives of the motion of the electron. Suppose that, leaving the meanings of $\mathbf{E}$ and $\mathbf{H}$ unspecified for the moment, we write

$$\mathbf{E} + \frac{[\mathbf{wH}]}{c} = \mathbf{W}, \quad . \quad . \quad . \quad . \quad . \quad (93)$$

so that

$$(\mathbf{E}.\mathbf{w}) = (\mathbf{W}.\mathbf{w}). \quad . \quad . \quad . \quad (94)$$

It then follows as a direct algebraical consequence that, since $k\mathbf{W}$, $ki(\mathbf{W}.\mathbf{w})/c$ is a 4-vector,

$$\mathbf{E}' + \frac{\mathbf{w}'\mathbf{H}'}{c} = \mathbf{W}', \quad . \quad . \quad . \quad . \quad . \quad (95)$$

$$(\mathbf{E}'.\mathbf{w}') = (\mathbf{W}'.\mathbf{w}'), \quad . \quad . \quad . \quad (96)$$

where $\mathbf{E}'$, $\mathbf{H}'$ are related to $\mathbf{E}$ and $\mathbf{H}$ by (90) and (91).

* These remarks concerned with the definitions of the quantities $\mathbf{S}$, S_t apply in similar fashion to the quantities $\mathbf{S}$, S_t of equations (13)–(16). It is important to notice that the fact that the charge is not conserved does not destroy its *invariance* in the sense of relativity theory. The forms of the equations provide for $\rho' d\tau' = \rho\, d\tau$ at corresponding instants, even though both of these quantities may vary with the time.

Now $\mathbf{W}$ involves constants and the time derivatives of the motion in the undashed system, and $\mathbf{W}'$ involves these in the same form in the dashed system. However, it is not to be concluded that (93) and (94) in transforming to (95) and (96) have remained invariant under the transformation in the practical sense unless we can show that $\mathbf{E}'$, $\mathbf{H}'$ and $\mathbf{E}$, $\mathbf{H}$ have corresponding meanings to the two observers in the two systems. In order to provide for this it is necessary to say what we intend to mean by $\mathbf{E}$ and $\mathbf{H}$. Thus, suppose we define $\mathbf{E}$ as the value of $\mathbf{W}$ when $\mathbf{w}$ is zero, and $\mathbf{H}$ as the limiting coefficient of $\mathbf{w}/c$ (taken in the sense of a vector product, with $\mathbf{w}$ directed so as to make the vector product a maximum) in the expression for $\mathbf{W}-\mathbf{E}$, when $\mathbf{w}$ is made infinitesimal *. Then obviously from equation (95) the corresponding definitions in the dashed system will make $\mathbf{E}'$ and $\mathbf{H}'$ the electric and magnetic fields in that system. Thus our definitions of $\mathbf{E}$ and $\mathbf{H}$ combined with the truth of such a relation as (93) have provided for a relation between the vectors in the two coordinate systems such as is given by (90) and (91). In other words, we have provided for a condition of affairs in which $\mathbf{H}$, $-i\mathbf{E}$ transforms as a 6-vector. It then follows that the right-hand side of (2) and the right-hand side of (3) with a factor i attached form a 4-vector, and the right-hand side of (4) and the right-hand side of (5) with a factor i attached form a 4-vector. Hence, since $\frac{\rho\mathbf{u}}{c}$, ρi form a 4-vector, the whole set of equations (2)–(6) is invariant, provided that the right-hand side of (6) satisfies the requirements that $\mathbf{W}$ must have †.

Some sort of an explanation may appear necessary for the apparently complicated definition of $\mathbf{E}$ given above. This definition is a generalization of the elementary definition of $\mathbf{E}$ in terms of the force on unit charge, a definition understood presumably in a vague sort of way as the mass

* Such definitions are closely in line with those which we should implicitly use in measuring $\mathbf{E}$ and $\mathbf{H}$ in terms of the motions of streams of electrons.

† It is important to observe that the procedure calls for the use on the right-hand side of (93) of such a quantity $\mathbf{W}$ that $k\mathbf{W}$ forms three components of a 4-vector whose fourth component is $ki(\mathbf{W}\cdot\mathbf{w})/c$. In the language of classical relativity the 4-vector must be perpendicular to the velocity 4-vector. The 4-vector $k\frac{d}{dt}k(\mathbf{w})$, $k\frac{d}{dt}(kic)$, whose first three components represent the generalization of the acceleration in the customary expression for $\mathbf{W}$, satisfies this condition, as shown in Appendix, Note 6.

acceleration of the charge. Strictly speaking, it is not possible to make a definition of $\mathbf{E}$ which involves only the acceleration of the electron when $\mathbf{w}=0$ regardless of what values the other derivatives may have. At least, any such definition would be useless for the purpose of building up such a relation as (93), since that relation certainly will involve, in general, all the other derivatives, even when $\mathbf{w}=0$. It is useless to say consider a case where all the derivatives of $\mathbf{w}$ are zero except $\dot{\mathbf{w}}$, for such a condition of motion would be, in general, inconsistent with the equation of motion proposed as regards its application at two consecutive instants.

Having defined $\mathbf{E}$, we might take equation (93) as the definition of $\mathbf{H}$ without restricting ourselves to the limiting case where $\mathbf{w}$ approaches zero. In this case the equation would be correct by definition. However, this procedure would not provide necessarily for the truth of (2)–(5) in terms of the $\mathbf{E}$ and $\mathbf{H}$ defined. The truth of these relations as holding between $\mathbf{E}$ and $\mathbf{H}$ defined in the manner stated would now constitute the fact of physics which the whole scheme expressed.

A knowledge of the form of the right-hand side of (93) and of the constants occurring in it is necessary for the purpose of making the definitions of $\mathbf{E}$ and $\mathbf{H}$ cited above. In the absence of any attempt to derive the whole scheme of equations from some unifying principle, the form in question, and the numerical constants in it, must be regarded as chosen in such a way that the $\mathbf{E}$ and $\mathbf{H}$ which become defined in terms of them satisfy (2)–(5). It is by no means certain nor likely that the choice of the form could always be made so that these equations are satisfied for any assigned distribution of ρ and $\rho\mathbf{u}$, and the assumption that it can constitutes the assumption implied in the whole scheme of equations.

Practically all that we have written with regard to the invariance of (2)–(5) may be said with regard to the invariance of (13)–(16) when taken in conjunction with a force equation such as (93). Any definitions of S_x, S_y, S_z, icS_t which provide for the 4-vector character of these quantities will insure the invariance of $S_t\,d\tau$. In general, the definitions would be founded upon the invariants peculiar to the form of $\mathbf{S}$, S_t. The idea becomes clear by considering the more general equations (25)–(28), with $\mathbf{S}$, S_t defined as in (23) and (24). Here, since $\rho\mathbf{u}$, ρic is a 4-vector, $\rho\,d\tau$ is invariant, as in the classical equations. Thus ρ may be defined by the two observers as the ratio of the invariant charge in the volume element to the magnitude of the

volume element. In such a case as that implied in equations (55)–(58), where $\mathbf{P}$, P_t, $\mathbf{Q}$, Q_t are expressed in terms of ρ and $\mathbf{u}$, no further definitions are necessary to complete their meaning. In other cases, where they might involve in their expression concepts other than electric density, as, for example, density of magnetism of one sign, the meaning of the new concept in question would have to be sought in terms of a definition based on whatever invariants were appropriate to the forms of the expressions.

Definitions of $\mathbf{E}_+$, $\mathbf{E}_-$, $\mathbf{H}_+$, $\mathbf{H}_-$, necessary to provide for the invariance of equations (25)–(35), may be made in the manner outlined above with slight complications depending upon the more elaborate forms of equations (33) and (34). Thus, let

$$k_+\mathbf{W}_+,\quad \frac{k_+ i}{c}(\mathbf{W}_+ . \mathbf{w}_+) \quad \text{and} \quad k_-\mathbf{W}_-,\quad \frac{k_-}{c} i(\mathbf{W}_- \ \mathbf{w}_-)$$

be 4-vectors specified in terms of the motion of the positive and negative electrons respectively. Then, holding in abeyance for a moment the definitions of $\mathbf{E}_+$, $\mathbf{H}_+$, $\mathbf{E}_-$, $\mathbf{H}_-$, let us write

$$\mathbf{W}_+ = \mathbf{E}_+ + \frac{[\mathbf{w}_+\mathbf{H}_+]}{c} + \lambda\left(\mathbf{E}_- + \frac{[\mathbf{w}_+\mathbf{H}_-]}{c}\right) \quad . \quad (97)$$

and

$$\mathbf{W}_- = \mathbf{E}_- + \frac{[\mathbf{w}_-\mathbf{H}_-]}{c} + \lambda\left(\mathbf{E}_+ + \frac{[\mathbf{w}_-\mathbf{H}_+]}{c}\right) . \quad (98)$$

Then, as a direct result of the 4-vector character associated with the W's, it follows that

$$\mathbf{W}_+' = \mathbf{E}_+' + \frac{[\mathbf{w}_+'\mathbf{H}_+']}{c} + \lambda\left(\mathbf{E}_-' + \frac{[\mathbf{w}_+'\mathbf{H}_-']}{c}\right), \quad (99)$$

$$\mathbf{W}_-' = \mathbf{E}_-' + \frac{[\mathbf{w}_-'\mathbf{H}_-']}{c} + \lambda\left(\mathbf{E}_+' + \frac{[\mathbf{w}_-'\mathbf{H}_+']}{c}\right), \quad (100)$$

where $\mathbf{E}_+'$, $\mathbf{H}_+'$, $\mathbf{E}_-'$, $\mathbf{H}_-'$ are defined in terms of the corresponding undashed vectors by relation of the forms (90) and (91). By putting $\mathbf{w}_+ = 0$ in (97), the equation serves to define $\mathbf{E}_+ + \lambda\mathbf{E}_-$. By putting $\mathbf{w}_- = 0$ in (98), the equation serves to define $\mathbf{E}_- + \lambda\mathbf{E}_+$. Hence both $\mathbf{E}_-$ and $\mathbf{E}_+$ are defined.

Then, by proceeding towards the limit when $\mathbf{w}_+ = 0$, in the manner adopted for the classical equations, (97) serves to define $\mathbf{H}_+ + \lambda\mathbf{H}_-$, since $\mathbf{E}_+$ and $\mathbf{E}_-$ are now defined; and in a similar way by proceeding towards the limit when $\mathbf{w}_- = 0$, (98) serves to define $\mathbf{H}_- + \lambda\mathbf{H}_+$. Hence $\mathbf{H}_-$ and $\mathbf{H}_+$ become defined.

From the similarity in form between (97) and (99) and between (98) and (100), it now follows that if the observer in the dashed system defines the fields in the way corresponding to that adopted by the observer in the undashed system, he will find the quantities $\mathbf{E}_+'$, $\mathbf{E}_-'$, $\mathbf{H}_+'$, $\mathbf{H}_-'$, and, as we have observed, these as related to the corresponding undashed quantities by the transformation of a 6-vector. The invariance of equations (25)–(32) then follows as before, since $\frac{\rho\mathbf{u}}{c}$, ρi constitute a 4-vector, and $\mathbf{S}_+$, $(S_t)_+$ constitute a 4-vector.

Note 6.—Since, to take one case which will represent all of its kind,

$$k_+\left(\mathbf{E}_- + \frac{[\mathbf{w}_+\mathbf{H}_+]}{c}\right) + \lambda k_+\left(\mathbf{E}_- + \frac{[\mathbf{w}_+\mathbf{H}_-]}{c}\right)$$

constitute three components of a 4-vector of which the fourth is

$$i\{k_+(\mathbf{E}_+ \cdot \mathbf{w}_+) + \lambda k_+(\mathbf{E}_- \cdot \mathbf{w}_+)\}/c,$$

it is obvious that this particular 4-vector has the property that its fourth component is i/c times the scalar product of $\mathbf{w}_+$ and its other three components. Hence any other 4-vector $k_+\mathbf{W}$, $k_+ic\mathrm{W}_t$ which is to be equated to it must have this property. In other words, we must have

$$k_+\mathrm{W}_t = k_+(\mathbf{W} \cdot \mathbf{w}_+)/c^2.$$

The acceleration 4-vector $k\frac{dk\mathbf{w}}{dt}$, $kic\frac{dk}{dt}$ has this property. For

$$\frac{i}{c}\left(\mathbf{w} \cdot k\frac{dk\mathbf{W}}{dt}\right) = \frac{i}{c}\left(kw_x\frac{dkw_x}{dt} + kw_y\frac{dkw_y}{dt} + kw_z\frac{dkw_z}{dt}\right)$$

$$= \frac{i}{2c}\frac{d}{dt}k^2(w_x^2 + w_y^2 + w_z^2)$$

$$= \frac{i}{2c}\frac{d}{dt}\left[\frac{q^2}{1 - q^2/c^2}\right] = \frac{ic}{2}\frac{dk^2}{dt} = ick\frac{dk}{dt}.$$

The property is not shared in general by the 4-vectors corresponding to the higher time derivatives so that, in the use of such an expression as (38), it is necessary that the invariant coefficients a, b, etc. shall be restricted by the requirement that the desired condition shall be satisfied by the 4-vector as a whole.

Note 7.—From a purely formal standpoint we may say that the content of the equations (25)–(34) with the relations (55)–(58) and with the understanding that the scheme of equations is to be invariant under the Lorentzian transformation and that the invariants α and β have been decided upon, is contained in the following statement. It is possible to assign to the volume elements of space, positive and negative numbers (the charges) which are the same for observers moving with constant relative velocity, and by dividing these numbers by the corresponding volume elements to define other numbers ρ_+ and ρ_-. Further, it is possible to assign to the volume elements vectors $\mathbf{u}_+$ and $\mathbf{u}_-$ (each transforming as a velocity) and other numbers and vectors associated with α and β in a way specified by the forms of these expressions, the numbers and vectors satisfying the conditions

$$\operatorname{div}(\rho_-\mathbf{u}_-)+\frac{\partial\rho_-}{\partial t}=0, \quad \text{and} \quad \operatorname{div}\mathbf{S}_+ + \frac{\partial(S_t)_+}{\partial t}=0.$$

Further, it is possible to assign a certain number λ and to assign to certain entities (protons and electrons) whose presence we believe we can detect, numbers e_+, e_-, m_+, m_-, such that if $\mathbf{E}_+$, $\mathbf{E}_-$, $\mathbf{H}_+$, $\mathbf{H}_-$, are calculated by (25)–(32) and the values when so determined are substituted in (33) and (34), these equations will give the motions of the observable entities.

It will be, of course, obvious from the above that, apart from the terms involving α and β, if we should, for example, multiply e_+, e_-, and all the ρ's by a constant factor η and the m's by η^2, the equations would serve to determine for the entities the same motions as before. Similar remarks apply in general when the terms in α and β are retained, the exact extent of the ambiguity in the numbers depending, however, upon the forms of the terms whose factors are α and β.

The numerical values of the constants m_+, m_-, e_+, e_-, etc. become fixed ultimately by a certain association with charge magnitudes defined in terms of mechanical force. Thus consider two parallel plates charged equally and negatively. The ordinary elementary theory of electrostatics leads to the expression $\mathrm{F}=\sigma^2/2$ for the force per unit area between the plates. In the spirit of the general standpoint outlined above, which left an ambiguity in the numbers e_+, e_-, etc., the expression $\mathrm{F}=\sigma^2/2$ is really a definition of the numerical value of σ in terms of F as measured mechanically. If we now form a picture of Millikan's oil-drop experiment as carried out in such a way that the field used is that due to one of the above plates, then, if f is the gain in the force on

the drop, measured mechanically, resulting from the acquisition of one electron, we have

$$f = X_- e_-,$$

where X_- is the field due to the charge density σ on the plate. Thus

$$f = \frac{\sigma}{2} e_- = \frac{\sqrt{2F}}{2} e_-, \quad . \quad . \quad . \quad . \quad (101)$$

which serves to determine the magnitude of e_-.

e_- having been determined, m_- becomes determined as $X_- e_-$ divided by the initial acceleration which the electron suffers in the field X_-, this field being measured as above. If one desires a degree of logical precision which requires specification of the other time derivatives of the motion besides the acceleration, one will be driven to the consideration of matters from the standpoint discussed in Appendix, Note 5.

For the determination of e_- and m_+ the procedure may be imagined as one similar to that outlined above, with the use, however, of a proton and a positively-charged plate* to produce the field. Such an experiment is, at the present time, an ideal one only. The incorporation of extra theoretical considerations such as belief in the equality of e_+ and e_-, and of the recognized structure of the hydrogen molecule as a means to obtain m_+, relieves us of the necessity for this ideal experiment.

Finally, λ becomes determined in terms of the gravitational constant G by equation (75). An ideal experiment, more closely in line with the significance of λ as it occurs in equations (33) and (34), is one in which the experiment on the determination of e_- is repeated with the field produced by a positively-charged plate. In this case equation (101) is replaced by $f = \frac{\sqrt{2F}}{2} \lambda e_-$, which serves to determine λ in terms of e_- as already determined. It need hardly be pointed out that the determination of λ by this procedure would be impracticable in view of the limits of experimental accuracy.

Absolute precision in the logical reasoning demands that, in the above, we pay attention to the gravitational attraction between the plates when measuring σ, and to the gravitational pull of the plate on the oil-drop and even on the electron

* The use of the positively-charged plate with the proton is only necessary formally in order to avoid the appearance of λ in the discussion at this point.

whose charge is being measured. These corrections are, of course, absolutely insignificant from the practical standpoint; but, in order to satisfy one who would feel confused as to the meaning of things until some ideal method of eliminating them had been *stated*, it will suffice to suppose that the experiment on the determination of e_- is carried out with successively larger charge densities on the plates and with successively smaller oil-drops. The value of e_- desired is then the limit corresponding to an infinitely large value of σ as above measured, and an infinitely small oil-drop.

Note 8.—Taking, for example, the motional effect on an initially stationary electron as the apparent measure of the electric field, that is as the measure appropriate for one who regards the laws of classical electrodynamics as exact, we see from (34) that the apparent field will be represented by

$$\mathbf{E}_- + \lambda \mathbf{E}_+ = \lambda(\mathbf{E}_+ + \mathbf{E}_-) + (1-\lambda)\mathbf{E}_-.$$

Here $\mathbf{E}_+$ and $\mathbf{E}_-$ are the fields due to all the positive and negative electricity in the neutral body. For the case where the body is at rest, $\mathbf{E}_-$ is the field calculated from all the negative electricity in the body on the basis of the law of inverse squares; and when the body is in motion with a velocity appreciably less than that of light, $\mathbf{E}_-$ has sensibly the same value as for the statical case. For the statical case, the term $(1-\lambda)\mathbf{E}_-$ represents merely the *gravitational* pull of the body on the electron, as will be evident on referring to the section on Gravitation. It is therefore negligible. Moreover, since λ is very nearly equal to unity, $\lambda(\mathbf{E}_+ + \mathbf{E}_-)$ may be replaced by $\mathbf{E}_+ + \mathbf{E}_-$. As a matter of fact, in the case which interests us, viz. that of uniform rotation, it turns out that $E_+ + E_-$ is sensibly zero for a neutral body, so that $(1-\lambda)\mathbf{E}_-$ is not necessarily negligible *compared* with it. However, in this case, as is shown in the text, we seek the electric field as resulting from an excess of negative over positive, that excess resulting from the death of positive electricity provided for by the equations. When compared with the electric field, for which we shall provide in this way, $(1-\lambda)\mathbf{E}_-$ is negligible.

Again, the force per unit charge on a negative electron moving in the absence of electric field is

$$\mathbf{F} = \frac{[\mathbf{w}_-\mathbf{H}_-]}{c} + \lambda\frac{[\mathbf{w}_-\mathbf{H}_+]}{c} = \lambda\left[\frac{\mathbf{w}_-}{c}.\mathbf{H}_+ + \mathbf{H}_-\right] + (1-\lambda)\frac{[\mathbf{w}_-\mathbf{H}_-]}{c}.$$

Now $\mathbf{H}_-$ is the magnetic field produced on the basis of the classical theory by the rotation of all the negative electricity in the body. For the case of the earth, it amounts at the pole to 2×10^{18} gauss. However, as shown in the section on Gravitation, $\lambda - 1 = 3{\cdot}9 \times 10^{-37}$. Hence the term $(1-\lambda)\frac{[\mathbf{w}_-\mathbf{H}_-]}{c}$ is negligible in any situation which provides for a value of $\mathbf{H}_+ + \mathbf{H}_-$ comparable with the earth's magnetic field. Further, since λ is nearly equal to unity, we have to a very high degree of approximation

$$\mathrm{F} = \left[\frac{\mathbf{w}}{c} . \overline{\mathbf{H}_+ + \mathbf{H}_-}\right].$$

If, then, we measure the apparent magnetic field $\mathbf{H}_0$ as the mechanical force divided by $\mathbf{w}_-$ when $\mathbf{w}_-$ is directed so as to make the force a maximum, the quantity we shall obtain for $\mathbf{H}_0$ will be equal to $\overline{\mathbf{H}_+ + \mathbf{H}_-}$.

Note 9.—For uniform rotation of a homogeneous body $\partial/\partial t = d/dt$. Moreover, as subsequently chosen in the section "Choice of the Invariants," the values of α and β given by (72) and (73) reduce for uniform rotation to

$$\alpha = \alpha_0 k_+^{-1}\omega^{-1}; \quad \beta = \beta_0 k_+ r^2\omega, \quad . \quad . \quad (102)$$

where α_0 and β_0 are constants. Hence, using (60), (62), (63), and (64), we have, from (51),

$$\frac{-\partial\rho_+}{\partial t} = -2\omega\alpha_0\rho_+ + \alpha_0\omega^{-1}\frac{\partial^2\rho_+}{\partial t^2} + \beta_0 k_+^3 r^2\omega\frac{\partial^3\rho_+}{\partial t^3} . \quad (103)$$

Now, while not necessary, it constitutes a simplification if we can neglect the last two terms on the right-hand side of (103). The procedure is justifiable if the solution for ρ_+ obtained from

$$\frac{-\partial\rho_+}{\partial t} = -2\omega\alpha_0\rho_+ \quad . \quad . \quad . \quad . \quad (104)$$

when substituted in the two terms in question makes them negligible in comparison with $2\omega\alpha_0\rho_+$. From (104) we obtain

$$\frac{\partial^2\rho_+}{\partial t^2} = 2\omega\alpha_0\frac{\partial\rho_+}{\partial t} = 4\omega^2\alpha_0^2\rho_+; \quad \frac{\partial^3\rho_+}{\partial t^3} = 8\omega^3\alpha_0^3\rho_+ \quad . \quad (105)$$

Substituting from (104) and (105) in the terms of (103) under discussion, we find that the ratio of their sum to $2\omega\alpha_0\rho_+$ is $2\alpha_0^2 + 4\beta_0\alpha_0^2 k_+^3\omega^3 r^2$. Now the values of α_0 and β_0

given by (70) and (74) respectively make the first term of this expression equal to $2{\cdot}9\times10^{-52}$ and the second term equal to $1{\cdot}8\times10^{-75}\omega^3r^2$; so that, even for such speeds as would make ωr equal to the velocity of light, this term only amounts to $16\times10^{-55}\omega$, and even for such angular velocities as are associated with atomic phenomena it is quite negligible. Thus for all practical purposes equation (103) may be replaced by (104), to which (65) is equivalent for the form of α given by (68).

Now, as regards the contributions of the terms $\alpha P'_t$ and βQ_t to the electric field of the rotating body, we have as follows:—

Using (60), (62), (104), (105), and (103), we have

$$\alpha P_t+\beta Q_t=\alpha k_+\frac{d\rho_+}{dt}+\beta k_+\frac{d^2\rho_+}{dt^2}$$

$$=-2\alpha_0{}^2\rho_++4\alpha_0{}^2\beta_0k_+{}^3\omega^3r^2\rho_+.$$

It is evident from (52) that, at any rate if we calculate the potential in the unretarded sense, $\alpha P_t+\beta Q_t$ acts exactly like a density of electricity ρ_0 given by

$$\rho_0=\alpha P_t+\beta Q_t=-2\alpha_0{}^2\rho_++4\alpha_0{}^2\beta_0k_+{}^3\omega^3r^2\rho_+,$$

or, putting $r=R_0\sin\theta$,

$$\rho_0=-2\alpha_0{}^2\rho_++4\alpha_0{}^2\beta_0k_+{}^3\omega^3R_0{}^2\rho_+\sin^2\theta.$$

It is, of course, easily possible to determine the field due to this distribution throughout the sphere. It is expressible as a series of spherical harmonics. However, we are concerned only with showing that the order of magnitude of the field is small. The order of magnitude of the field will be the same as that calculated by putting $\sin\theta=1$ everywhere; and, of course, putting $k_+=1$. In this way we obtain for the field at the surface a quantity of the order

$$E_0=\frac{8\pi\alpha_0{}^2\,Dea}{m}\left(\frac{2\omega^3a^2\beta_0}{5}-\frac{1}{3}\right),$$

where we have replaced ρ_+ by De/m, D being the earth's density, e the charge on the proton, and m the sum of the masses of a proton and an electron. E_0 as expressed above is in electrostatic units if e is in electrostatic units. Using the value of α_0 given by (70), the value of β_0 given by (74), and the data for ω, D, and a given just prior to equation (74), we find, for the earth,

$$E_0=-1{\cdot}2\times10^{-27}\text{ e.s.u.},$$

a quantity insignificant compared with the earth's potential

gradient of about 150 volts per metre for which the theory provides otherwise.

If we had used in (52) the retarded values in the numerator, the value of ρ_0 assigned to any volume element would have differed from the value used above by a quantity $\Delta\rho_0$, which is such that

$$|\Delta\rho_0| < \left|\frac{2a}{c}\left(\frac{\partial\rho_0}{\partial t}\right)\right|,$$

where $2a/c$ represents the time for light to travel a distance equal to the diameter of the sphere. Thus

$$\left|\frac{\Delta\rho_0}{\rho_0}\right| < \left|\frac{2a}{c\rho_0}\left(\frac{\partial\rho_0}{\partial t}\right)\right|,$$

or, using (104),

$$\left|\frac{\Delta\rho_0}{\rho_0}\right| < -4\frac{a\omega\alpha_0}{c}.$$

Even for a value of $a\omega$ equal to the velocity of light, $\Delta\rho_0/\rho_0|$ is only $-4\alpha_0$, *i. e.* $4{\cdot}8\times10^{-26}$. Thus the effect of using the unretarded in place of the retarded potential is negligible in its influence on the field E_0 calculated above, which field E_0 is negligible, as we have seen.

Turning now to the contribution of the term

$$-\frac{1}{c}\frac{\partial}{\partial t}(\mathbf{U}_+ + \mathbf{U}_-)$$

in equation (54), it is only because of the slight departure from a steady state caused by the slow death of the positive electricity that this term makes any contribution at all. The magnitude $\delta\mathbf{E}$ of the contribution is certainly less than that which we should calculate if we should assign to each volume element in (53) vectors equal in magnitude to the absolute values of $\alpha\mathbf{P}$ and $\beta\mathbf{Q}$ but in the same direction, and, moreover, in the same direction for each volume element. The absolute value which we should calculate for the integral in (53) by using such a process would be 4π times the potential $\dot{V}$ due to a distribution ρ_1 given by *

$$\rho_1 = |\alpha P| + |\beta Q|,$$

and we should thus have

$$|\delta E| < \left|\frac{1}{c^2}\frac{dV}{dt}\right|. \quad . \quad . \quad . \quad . \quad . \quad (106)$$

The use of unretarded values in calculating V does not, of course, affect the order of magnitude.

* We shall omit clarendon type in absolute values.

Using (59), (61), and (102), we have

$$\rho_1 = (\alpha_0 r\omega + \beta_0 k_+^{\,3} r^3 \omega^4)\rho_+.$$

The potential at a point due to this distribution is of the same order of magnitude as that obtained by putting $k_+ = 1$, replacing r by $R_0 \sin\theta$, R_0 being the radius vector from the centre of the sphere, and then discarding everywhere the difference between $\sin\theta$ and unity. With these approximations we find for V at a point on the surface of the sphere of radius a:

$$\begin{aligned} V &= \frac{1}{a}\int_0^a (\alpha_0 \omega R_0 + \beta_0 \omega^4 R_0^{\,3})\rho_+ R_0^{\,2}\, dR_0 \\ &= \tfrac{1}{4}(a^3\alpha_0\omega + \tfrac{2}{3}a^5\omega^4\beta_0)\rho_+. \end{aligned}$$

Thus, using (104) and (106) and putting $\rho_+ = De\ m$, we have

$$|\delta E| < \left| \frac{2\omega^2\alpha_0^{\,2}a^3\pi}{e^2}\left(1 + \tfrac{2}{3}a^2\frac{\beta_0}{\alpha_0}\omega^2\right)\frac{De}{m}\right|,$$

where e is in e.s u., and we have introduced the factor 4π, so that δE is in e.s.u. Putting in the values appropriate for the earth, we find

$$|\delta E| < 6{\cdot}2 \times 10^{-32} \text{ e.s.u.},$$

which is insignificant compared with the earth's potential gradient.

Note 10.—If the whole of the positive electricity in the earth were rotating alone as a solid mass with the earth's angular velocity, the ordinary current density, which would be tangential, would amount at any point to $r\omega\rho_+$. A fraction 5×10^{-19} of this current density would give rise to a field comparable with that of the earth. Now, using (59) and (68),

$$\alpha P = \alpha r\omega\rho_+,$$

and, from (70),

$$\alpha P = 1{\cdot}2 \times 10^{-26}(r\omega\rho_+) = 2{\cdot}4 \times 10^{-8}(r\omega\rho_+ \times 5 \times 10^{-19}).$$

Hence the apparent radial current density at any point is only $2{\cdot}4 \times 10^{-8}$ of the tangential current density which would apply to that point in a current distribution of density proportional to the distance from the axis of rotation and of amount such as to produce a magnetic field equal to that of the earth.

Again, as regards the retarded feature in (53), following a line of argument similar to that used in Note 9, and using

(59), (61), and (104), we have that the errors in P and Q resulting from failure to take account of the retarded feature are ΔP and ΔQ, such that

$$\left|\frac{\Delta P}{P}\right| = \left|\frac{\Delta Q}{Q}\right| < 2\frac{a}{c}\omega\alpha_0,$$

so that since $a\omega$ must be less than c, each of these quantities is less than $2\alpha_0$, and is therefore exceedingly small. The effect of $\Delta\mathbf{P}$ on the contributions of $\alpha\mathbf{P}$ from each volume element is consequently exceedingly small compared with that contribution itself, which we have already found negligible. The only effect of $\Delta\mathbf{Q}$ is to change our calculation of $\mathbf{U}_+ + \mathbf{U}_-$, and consequently of $\mathbf{H}_+ + \mathbf{H}_-$, to an exceedingly small extent as a result of a very slight change in the apparent current density to be assigned to each volume element of the sphere.

Note 11.—In virtue of (33) and (34), the combined force on a unit of positive and a unit of negative charge moving with equal velocity $\mathbf{w}$ is

$$\delta\mathbf{F} = (1-\lambda)\left(\mathbf{E}_+ - \mathbf{E}_- + \frac{[\mathbf{w}.\mathbf{H}_+ - \mathbf{H}_-]}{c}\right).$$

Here $\mathbf{E}_+ - \mathbf{E}_-$ and $\mathbf{H}_+ - \mathbf{H}_-$ really represent additions of quantities of like signs, since $\mathbf{E}_+$ and $\mathbf{H}_+$ represent the field due to all the positive electricity in the piece of matter, and $\mathbf{E}_-$ and $\mathbf{H}_-$ represent the field due to the corresponding negative electricity.

Now, $\mathbf{E}_+$ and $\mathbf{H}_+$ are very nearly equal to the values calculable on strict classical theory, so that, to a high degree of approximation, for a neutral body,

$$\delta\mathbf{F} = -2(1-\lambda)\left\{\mathbf{E}_- + \frac{[\mathbf{w}\mathbf{H}_-]}{c}\right\},$$

$\mathbf{E}_-$ and $\mathbf{H}_-$ being, of course, calculable on the classical theory. Now it is easy to see, and is well known, that $\mathbf{H}_-$ is of the order $\mathbf{w}/c$, so that, up to and including the order $\mathbf{w}/c$,

$$\delta\mathbf{F} = -2(1-\lambda)\mathbf{E}_-.$$

Further, as is well known, $\mathbf{E}_-$ differs from the field calculable on the basis of pure electrostatics only by quantities of the order $\mathbf{w}^2/c^2$. Hence, to a high degree of approximation, the force on an element of matter $d\tau_2$ containing N_2 protons and N_2 electrons per c.c. and due to an element of

matter $d\tau_1$ containing N_1 protons and N_1 electrons per c.c., is

$$\delta F = \frac{2N_1N_2e^2}{R^2}(1-\lambda)\,d\tau_1\,d\tau_2,$$

where e is in electrostatic units.

Sloane Laboratory,
Yale University,
April 8, 1926.

CX. *Precision Measurement of the* K-*Series of Molybdenum and Iron.* *By* Axel Larsson *.

[Plates XV.–XVIII.]

In the following article is given a detailed description of a precision spectrograph developed at the Physical Laboratory of the University of Upsala, and intended for a wave-length range of 0·4–2·5 Å.U. In addition, results are given of the measurement of the K-series of iron and molybdenum.

Introduction.

As is well known, Professor Siegbahn has constructed, first at the Lund Physical Laboratory and recently at Upsala, a number of spectrographs for the precision measurement of the wave-lengths of X-rays. These instruments are constructed in conformity with various principles, according to the degree of hardness of the rays. The type of photographic spectograph based on the principle most suitable for the wave-length range 0·4–2·5 Å.U. was developed in 1919 †.

In accordance with this principle there was constructed at the Upsala Physical Institution in 1925 an improved spectrograph of this type, and this instrument was used by Siegbahn and Hjalmar ‡ for the measurement of the $K\alpha_1$ line of copper. In order to carry the precision as far as possible, however, the construction of a spectrograph of the same type but equipped with better facilities for adjustment and furnished with a considerably better circular scale was

* Communicated by Prof. Manne Siegbahn, D.Sc.

† M. Siegbahn and A. Leide, Phil. Mag. ser. 6, vol. xxxviii. p. 647 (1919).

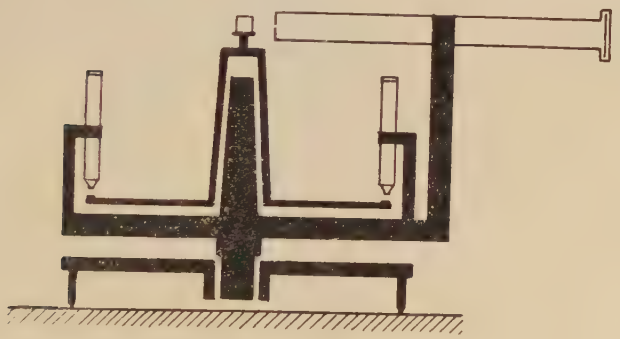
‡ M. Siegbahn and E. Hjalmar, *Ark. f. Mat. Astron. Fys.* xix. A. No. 24 (1925).

begun immediately afterwards. The writer assisted Professor Siegbahn in the construction of this spectrograph, and by means of it carried out a precision determination of the wave-lengths of the K-series of molybdenum and iron. As no full account of this type of spectrograph has hitherto been published, there is given in the following a more detailed description of its construction, adjustment, and method of operation.

Principle of Measurement.

The principal features of the spectrograph are evident from fig. 1. It consists of three rigid units. The under

Fig. 1.



part serves only as a base, which by means of a vertical bearing supports the spectrograph proper, comprised by the other two systems. The essential parts of one system are the microscope, the slit, and the photographic plate. The remaining system, the essential parts of which are the precision scale and the crystal, can be rotated around the second system by means of a conical bearing.

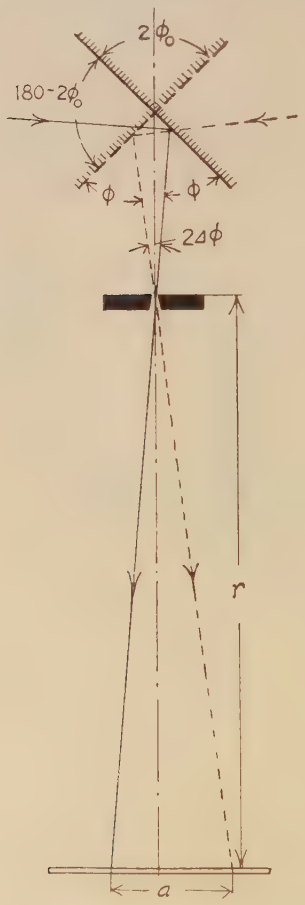
Fig. 2 shows the method of measurement. With the crystal in position 1 (solid lines) the line whose wave-length is to be determined is exposed on the plate. The position of the crystal with respect to the plate is read off accurately by means of the microscopes. After this the crystal is adjusted to position 2 (dotted lines), which is so chosen that when the X-ray line concerned is exposed, the line on the plate falls in the immediate proximity of the line obtained in position 1. Position 2 is read off by means of the microscopes. The difference between positions 1 and 2

is $180° - 2\phi_0$. The difference between ϕ_0 and the angle of reflexion ϕ is $\Delta\phi$, and thus

$$\phi = \phi_0 + \Delta\phi.$$

The small angle $\Delta\phi$ is determined by measuring the

Fig. 2.



distance between the lines on the plate ($=a$ mm.) and also the distance from slit to plate ($=r$ mm.), and is calculated according to the equation

$$2\Delta\phi = \frac{a}{r}.$$

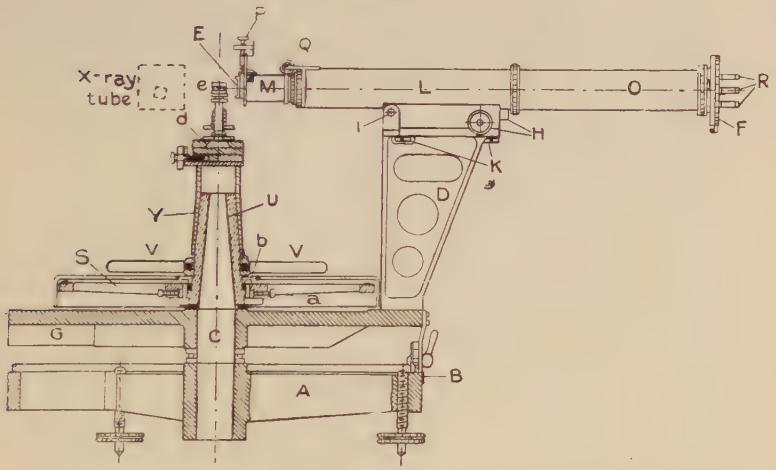
According to fig. 2, which is intended to represent the

principle of measurement, the X-ray tube should be displaced through an angle of about 4ϕ between the two exposures. Since this would cause great inconvenience, the X-ray tube is kept in the original position and instead the spectrograph is rotated through this angle. This is easily accomplished by means of the vertical bearing in the base.

Construction of the Spectrograph.

Fig. 3 represents the construction of the spectrograph in detail. Fig. 4 (Pl. XV.) is a photograph of the spectrograph with the adjusting equipment, and figs. 5 and 6

Fig. 3.



(Pls. XVI. & XVII.) show the spectrograph with the X-ray tube and the pumps.

As seen by the above orientating description, the spectrograph consists of three rigid systems which may be rotated with respect to one another. The under part (A) is the cast-iron base. This carries the spectrograph proper by means of a vertical bearing and an axial ball-bearing, the weight being borne by the latter. The base is provided with three adjustable feet. On its upper rim is mounted a circular scale graduated in whole degrees (B), on which the rotation of the upper systems can be read. On the upper surface of the outer ring is mounted a turned flange to which the upper systems can be locked.

The middle system consists of a heavy steel axle (C) to

which is attached a head with four heavy ⊔-shaped arms, mounted at right angles. The head and arms are cast in one piece. The microscopes are attached to two diametrically-opposed arms. To one of the remaining arms is screwed a cast-iron, vertical arm (D) of I-section, which carries the camera. At the inner end of this camera is a slit (E), and at the outer end a plate holder (F). To the fourth arm is attached a lead counterbalance (G) for the camera. It is of the greatest importance for the accuracy of measurement that no deformation of the system take place during an exposure. For this reason all the parts are very heavily proportioned. It may be remarked that defects in the stability of the base and bearings do not affect the accuracy of measurement.

The camera is so attached to the vertical carrying-arm that the distance of the entire camera from the crystal can be regulated by means of a rack and pinion (H). In addition, there are screws (I) for lateral adjustment of the camera. Once adjusted in the desired position, it can be locked by means of special screws (K). The camera consists of three different tubes : a central tube (L) carried by the vertical arm, a front tube (M) to which the slit is attached, and an extension tube (O) to which the plate-holder is screwed. Two different lengths of this latter tube are provided ; the shorter is shown *in situ* in figs. 4 and 5 (Pls. XV. & XVI.). The plate-holder may also be screwed directly on to the central tube, so that three different distances between the slit and the plate are available.

The width of the slit is varied through displacing the edges of the slit in a wedge-shaped slide by means of a vertical screw (P). As the screw is provided with a graduated head, the desired width of slit can easily be obtained. One division on the graduated head corresponds to a slit width of 0·00075 mm. Also the length of the slit can be arbitrarily varied by means of a wedge-shaped diaphragm-opening superposed on the slit. For the adjustment of the slit parallel to the axis of rotation, the entire slit-system can be rotated round a horizontal axle by means of a tangent-screw (Q). The construction is carried out in such a way that the distance of the slit from the plate is not altered through this operation.

On account of the high demands on the accuracy of measurement, the length of the camera must be completely defined ; *i.e.*, the slit must have sharp edges. Since, however, the spectrograph is designed for quite hard radiations, the angle of opening must be small (5°) in order

that sharp lines may be obtained, and for the material of the slit must be chosen a metal with high atomic number (platinum).

To insure that the photographic plates always assume the same position in the plate-holder, they are held against three bosses by means of spiral springs (R). Two of these bosses are placed in the vertical plane of symmetry, and the third at one side. In addition, the plate-holder is provided with cross-hairs of very fine tungsten wire, and also a metal slide operated from the outside, by means of which different portions of the lines may be screened off. With the aid of this arrangement, one can easily decide which lines have been exposed in one or another position of the crystal. Visible light is excluded from the plate-holder by a diaphragm of black paper placed in the interior of the camera.

The system consisting of the precision scale (S) and crystal table is separated from the above-described system by means of a conical bearing (U). The upper system may be turned round the spindle by means of four horizontal arms (V), which are attached at right angles to the upper system. The two systems may be locked to each other by means of a screw. After this a very accurate adjustment can be made through a micrometric rotation of the upper system by means of a tangent screw. This arrangement is seen on the photographs, figs. 4 and 5 (Pls. XV. & XVI.).

The turning and grinding of the conical bearing was carried out with great care. The lubricating medium used in this bearing must likewise conform to very strict specifications. The crystal table can be rotated with respect to the scale by means of an outer conical bearing (Y). This arrangement, however, is to be made use of only when it is desired to use different parts of the precision scale. In the case of the outer bearing, the grinding and turning need not be carried out with as great care as that of the inner one.

The precision scale (S) was made by the Askania Werke, Berlin. Its diameter is 40 cm., and it is graduated in $5'$ intervals. The graduations are on the upper face. The microscopes belonging to the scale are provided with 45° total-reflecting prisms, and for this reason are mounted in horizontal and radial positions. They are equipped with ocular micrometers, every scale-division on the graduated head being equivalent to $1''$. Thus readings may be made to $0''{\cdot}1$. The microscopes may be raised and lowered by means of a rack and pinion operating in a slide, which is provided with an effective locking-screw (see the photographs, figs. 4 and 5, Pls. XV. & XVI.). The microscope mounting

in its entirety is very stably constructed. Small electric lamps are used to illuminate the scale.

For the centring of the scale four radially-mounted screws (*a*) are provided. After adjustment the scale is locked by means of special screws (*b*). Both the scale and the microscopes are surrounded by a metal screen. The crystal table is provided with two horizontal slides (*d*) mounted at right angles to one another ; this makes possible an arbitrary displacement of the crystal (*e*). These slides were made with such care that all risk of a displacement of the crystal after adjustment is obviated. The screws used on these slides are provided with graduated heads, on which the amount of displacement can be read. It is evident from the drawing that the elevation of the crystal can easily be changed. The inclination of the crystal can be altered by means of a screw, and when it has been adjusted it is held in fixed position by a spring. The construction is seen on fig. 4 (Pl. XV.).

Construction and Operation of the X-ray Tube.

The X-rays are generated in a metallic X-ray tube of cubical form with hot cathode, constructed by Prof. Siegbahn. The appearance of this tube may be seen from figs. 5 and 6 (Pls. XVI. & XVII.). The tube, which is completely isolated from the spectrograph, is mounted on a stable base, and can be raised or lowered by means of a heavy steel screw. Cooling is accomplished by means of oil, circulated by a geared pump, and the oil in turn is cooled by water. This arrangement has proved to be especially advantageous. The source of high tension was a single-armatured converter with transformer and mechanical rectifier. The voltage was held at about 50 kv., and the current at about 8 milliamperes.

Adjustment of the Spectrograph.

A. *Adjustment of the Precision Scale and Microscopes.*

The precision scale is centred by taking readings with both microscopes in a certain number of positions, the intervals between the positions being equal for a given revolution. If the scale is rightly centred, the difference between the readings of the two microscopes should be constant. If a certain eccentricity exists, it is to be detected from the sine form of the curve obtained when the differences between the microscope readings are plotted as ordinates against the readings of one of the microscopes

as abscissæ. From the shape of this curve one can, knowing the pitch of the adjusting screws, so displace the scale that the eccentricity is reduced to a minimum. Such an eccentricity involves no errors in measurement, as readings are taken with both microscopes. The magnification of the microscopes is so regulated that one division on the scale of the ocular micrometer is equivalent to 1″. Further, minor errors in this connexion have been eliminated through the method of measurement employed (*cf.* below).

B. *Adjustment of the Camera.*

The "axis" of the camera may be defined as the straight line through the centre of the plate-holder (cross-hairs) and the centre of the slit, the latter being fixed by the position of the apex of the wedge-shaped diaphragm-opening. The purpose of this adjustment is to bring the camera into such a position that its axis (1) cuts the axis of rotation of the crystal, and (2) is at right angles to the same. Furthermore, the slit must be parallel with the axis of rotation of the crystal.

First the axes are adjusted to right angles with each other. On the crystal table is placed a mirror, which is so adjusted that its reflecting surface is parallel to the axis of rotation of the crystal system. This is done in such a way that a plane-parallel glass plate extending somewhat above the mirror is pressed against it. A telescope with vertical millimetre scale is then set up at a distance of about one metre, and the height of the mirror-image of the scale from the plane-parallel glass plate is observed in the telescope with the aid of the cross-hairs. The crystal table is then turned through 180° and a new reading taken. The adjusting-screw is turned sufficiently to give similar readings upon reversing the position of the crystal table. In the plate-holder is inserted a metal plate with a horizontal slit at the same height as the cross-hairs. The length of the X-ray slit is so diminished that it is quite short. The light from a lamp passes through both slits, and the mirror on the crystal table reflects it back through the X-ray slit into the camera. The metal plate in the plate-holder is held in such a position that the point of incidence of the reflected light can be observed on its back side. By placing a piece of metal foil of suitable thickness under the base of the vertical supporting arm of the camera, the chamber can be brought into such a position that the reflected light strikes the plate in the same *niveau* as the slit.

The X-ray slit is then adjusted in such a way that its length is parallel to the axis of rotation of the crystal. In the slit is inserted a small glass plate whose sides are parallel to the edges of the slit. The camera and crystal table are so rotated that in the above-mentioned observation telescope the image of the scale can be observed both on the mirror, which has previously been adjusted parallel to the axis of rotation, and on the glass plate inserted in the slit. The slit-system is rotated until both mirror-images coincide; it is obvious that the adjustment is then complete.

In order to cause the "axis" of the camera to cut the axis of rotation, the mirror is removed from the crystal table, and in its place is fastened a small slide provided with a fine wire. The crystal table is displaced by means of its slides so that the wire coincides with the axis of rotation. The wire is observed through a microscope mounted in a horizontal position.

In the plate-holder is placed a metal plate with vertical slit, which falls directly in front of the cross-hairs. The light from a lamp is passed through this slit and the X-ray slit, in the direction towards the wire. The wire, as well as the interference bands of the light emanating from the narrow X-ray slit, is observed from the opposite direction by means of a microscope. With the adjusting-screws (I) mentioned in the above description of the apparatus, the camera is adjusted laterally until the interference bands appear to be symmetrically distributed around the wire, whereupon the camera is locked in this position. The camera is then displaced longitudinally by means of the rack and pinion, and it was observed that the axis of the camera always cuts the axis of rotation. Errors in placing the X-ray slit when adjusted by this method do not exceed 0·005 mm.

C. *Adjustment of the Crystal.*

The purpose of this adjustment is partly to bring the atomic planes parallel to the axis of rotation and partly so to locate the crystal that its limiting surface coincides with the axis of rotation. The crystal used in this case had a columnar, unpolished surface measuring 1×8 mm. It was fitted and cemented into a metal mounting, which in turn was screwed fast to the crystal table.

The crystal is adjusted to the proper height with the help of the plate having the horizontal slit. This plate is placed in the plate-holder and the X-ray slit is screened off to a short length. Since the light from a lamp passes both slits

and strikes the crystal, the crystal can easily be adjusted to the proper height.

A preliminary adjustment for the purpose of bringing the atomic planes parallel to the axis of rotation is made in such a way that the above-mentioned plane-parallel glass plate is pressed against the crystal surface and brought parallel to the axis by the aid of a telescope and scale, as described above. It is evident, however, that if small step-like ledges are present on the cleavage surface of the crystal, the above-mentioned method does not lead to the desired result, and an after-correction must be made. Upon making a double exposure of a certain X-ray line, as described in the section dealing with the method of measurement, the lines do not become fully parallel if the atomic plane is not parallel to the axis of rotation. By measuring the mutual inclination of the lines (about 2′), the correction of the crystal necessary for parallelism may be calculated. The amount of rotation is read off with the help of a telescope with scale, and a mirror placed on the crystal table in front of the crystal. The parallelism of the lines in such a double exposure is a certain criterion for the parallelism of the atomic plane and the axis of rotation.

The adjustment of the crystal surface in the axis of rotation is performed with the help of an apparatus shown in fig. 4 (Pl. XV.), which is screwed fast to the under-fixed part of the crystal table. This apparatus is provided with a fine bone point directed towards the crystal. It may be moved back and forth by means of a screw, and a tangent-screw is provided for lateral adjustment. After this apparatus has been placed at the proper height, the bone point is adjusted so that it coincides with the axis of rotation of the crystal. This is accomplished by observing the position of the point through a microscope, during rotation of the crystal system. The microscope is held by a special mounting attached to the base of the spectrograph (see fig. 4, Pl. XV.). When the point coincides with the axis of rotation, the crystal is advanced towards the point until the point and its mirror-image on the crystal surface are just tangent to each other; this can be observed accurately in the microscope. The error involved in this adjustment does not in this case exceed 0·002 mm.

Measurement of the Distance from Slit to Plate.

In the plate-holder is inserted a metal plate bearing a raised, somewhat rounded plug (see fig. 4, Pl. XV.). Over the camera is fastened a metal mounting which serves as

support for the metal slide (see fig. 4, Pl. XV.) with which the distance is measured. This slide is provided with two bone points, of which one is pressed lightly against the slit and the other against the plug inserted in the plate-holder. The points are then fastened in these positions. The distance between the points is obtained by placing the slide over a normal metre and measuring the distance between the points to the nearest divisions on the normal metre with the help of a dividing engine. The length of the metal plug inserted in the plate-holder is measured with a micrometer-screw. The length of the camera is obtained by subtracting this length from the distance between the points. The absolute error in the length of the camera when measured in this way does not exceed 0·04 mm.

Adjustment of the Position of the X-ray Tube.

As to judging the accuracy of measurement, it will be seen in the following that the focus-spot on the anticathode must be adjusted to the proper height; *i. e.*, it must be in the same *niveau* as the axis of the camera. The vertical extension of the focus-spot is slight. A fluorescent screen is placed in the plate-holder and the height of the X-ray slit is screened off to about 1 mm. The X-ray tube is adjusted to such a height that the narrow bundle of X-rays falls directly in front of the cross-hairs. The zero-position of the camera is read off the same time.

Carrying out of the Precision Measurement.

A preliminary exposure is made to determine the zero-position of the crystal; *i. e.*, the position that is read off on the precision scale when the crystal surface coincides with the axis of the camera.

In the following will be given a detailed account of the determination of the angle of reflexion of the $K\alpha_1$ lines of molybdenum. The crystal used was of calcite, marked K.N.2. The numerical data are taken from the exposure of plate S.L.19. The width of the slit was 0·02 mm., as in all determinations of molybdenum. The two positions of the double exposure are indicated by R and L, since the reflexion from the crystal is bent to the right or to the left when viewing the spectrograph from the X-ray tube. From foregoing determinations we know the approximate value of the angle of reflexion $=6^\circ\,42'\,35''$. In order that the two lines of the double exposures may not coincide, however, the somewhat smaller value of $6^\circ\,40'$ is taken for determining

the position of crystal and camera. Since the zero-position of the crystal, read off with microscope A, is 205° 55′, the adjustment of the crystal thus becomes approximately

in position R : 205° 55′ − 6° 40′ = 199° 15′

and in position L : 205° 55′ + 6° 40′ + 180° = 32° 35′.

Since the zero-position of the plate-holder is 340°, this becomes upon adjustment

in position R : 340° − 2 × 6°·7 = 326°·6

and in position L : 340° + 2 × 6°·7 = 353°·4.

But in order that radiations from different points of the focus-spot may be effective, the adjustment of the plate-holder is changed several times during exposure, through an interval of about 1°. The adjustment of the plate-holder may thus be written

in position R: 326°·1 to 327°·1

and in position R : 352°·9 to 353°·9.

After the adjustment in position R has been completed and the crystal system has been locked in place, the position of the crystal with respect to the plate-holder is read off with the two ocular micrometers. Five successive divisions at 5′ intervals on the precision scale are read off with each microscope, each reading being taken three times. The position of the crystal is thus established by means of 30 readings. The following readings were taken with microscope A :—

° ′ ″	° ′ ″	° ′ ″	° ′ ″	° ′ ″
199 5 7·0	199 10 5·5	199 15 6·0	199 20 7·0	199 25 6·5
7·5	6·0	6·5	7·0	6·0
7·2	6·5	6·7	7·0	6·2

Average : 199° 15′ 6″·6.

With microscope B :—

° ′ ″	° ′ ″	° ′ ″	° ′ ″	° ′ ″
19 5 41·8	19 10 43·1	19 15 44·2	19 20 45·3	19 25 46·6
41·8	42·6	44·8	45·1	46·6
41·4	43·4	44·9	45·2	46·7

Average : 19° 15′ 44″·2.

After 15 minutes' exposure at 45 kv. and 7 milliamp., the adjustment to position L was made.

Readings with microscope A :—

32° 25′ 9″·6	32° 30′ 7″·8	32° 35′ 8″·0	32° 40′ 8″·0	32° 45′ 7″·8
9·8	8·2	8·5	7·6	7·2
9·5	7·6	7·8	7·8	7·0

Average : 32° 35′ 8″·2.

With microscope B :—

212° 30′ 44″·0	212° 35′ 46″·2	212° 40′ 46″·8
43·8	46·2	45·8
44·3	45·5	46·0

212° 45′ 47″·8	212° 50′ 49″·5
47·5	48·5
47·0	48·5

Average : 212° 40′ 46″·5.

The observed values at $2\phi_0$ thus become :—

With microscope A :

$$32^\circ\ 35'\ 8''{\cdot}2 + 180^\circ - 199^\circ\ 15'\ 6''{\cdot}6 = 13^\circ\ 20'\ 1''{\cdot}6.$$

With microscope B :

$$212^\circ\ 40'\ 46''{\cdot}5 - 180^\circ - 19^\circ\ 15'\ 44''{\cdot}2 = 13^\circ\ 20'\ 2''{\cdot}3.$$

The average value being

$$2\phi_0 = 13^\circ\ 20'\ 2''{\cdot}0.$$

It may be remarked that, apart from minor observation errors, the variations in the values obtained with the two microscopes may to a large degree be ascribed to the somewhat eccentric position of the precision scale.

The temperature, both before and after exposure, was 19°·6 C.

The distance between the lines (a mm.) was measured directly in front of the shadow of the cross-hairs on the plate. For this purpose a Gaertner Comparator was used. Readings were taken to 0·0001 mm. The doublet distance $K(\alpha_1 - \alpha_2)$ was measured at the same time.

In the various determinations the deviations from the mean are nowhere greater than 0·001 mm. Possible errors in the screw of the comparator were eliminated by using different parts of the same. The distance between the lines

was always measured 10 to 20 times. In this case the average value obtained was

$$a = 0{\cdot}6460 \text{ mm.}$$

When the distance from slit to plate was

$$r = 432{\cdot}76 \text{ mm.},$$

the value $2\Delta\phi = 5'\ 7''{\cdot}9.$

At a temperature of 19°·6 C. the glancing-angle is thus

$$\phi = 0{\cdot}5\ (13°\ 20'\ 2''{\cdot}0 + 5'\ 7''{\cdot}9) = 6°\ 42'\ 35''{\cdot}0.$$

The temperature was read to 0°·1, using two thermometers placed on opposite sides of the crystal. From what we know about the transfer of energy in the anticathode, and also when the X-rays strike the crystal, it is evident that the temperature of the crystal cannot be appreciably higher than that of the surroundings.

The angles of reflexion have been reduced to one and the same temperature, namely 18° C. The following symbols are used:—

ϕ_{18} = angle of reflexion at 18° C.
ϕ = angle of reflexion at t° C.
$d\phi$ = change in angle.
d = lattice constant.
Δd = lattice constant's alteration due to change in temperature $(t-18)$° C.
α = crystal's coefficient of linear expansion at right angles to the atomic plane.

We write $\phi_{18} = \phi - d\phi.$

By differentiation of Bragg's equation $n\lambda = 2d \sin\phi$ we get

$$d\phi = -\frac{\Delta d}{d} \cdot \tan\phi;$$

but $\Delta d = \alpha d(t-18),$

and since $\alpha = 0{\cdot}0000104,$

we get for calcite, if $d\phi$ is expressed in seconds,

$$d\phi = 2{\cdot}15(18-t)\tan\phi.$$

In this case we have

$$d\phi = -0''{\cdot}4;$$

therefore $\phi_{18} = 6°\ 42'\ 35''{\cdot}4.$

Table I.

Absolute measurements in first order.

Plate.	Line.	Temp.	$2\phi_0$.	a (mm.).	$2\Delta\phi$.	ϕ_t.	ϕ_{18}.	λ (X.U.).	$\bar{\lambda}$.
		°	° ′ ″		′ ″	° ′ ″	° ′ ″		
S.L. 19	Mo $K\alpha_1$	19·6	13 20 2·0	+0·6460	5 7·9	6 42 35·0	6 42 35·4	707·833	
,, 20	,,	18·2	13 29 59·4	−0·6068	4 49·2	6 42 35·1	6 42 35·2	707·827	
,, 27	,,	19·9	13 30 1·1	−0·6110	4 51·2	6 42 35·0	6 42 35·5	707·836	
,, 29	,,	20·5	13 19 59·9	+0·6492	5 9·4	6 42 34·7	6 42 35·3	707·830	
,, 37	,,	19·2	13 20 2·2	+0·9276	5 7·6	6 42 34·9	6 42 35·2	707 827	707·831
,, 21	Mo $K\beta_1$	18·8	11 55 0·0	+0·3025	2 24·2	5 58 42·1	5 58 42·3	630·972	
,, 22	,,	18·5	11 54 59·7	+0·3051	2 25·4	5 58 42·6	5 58 42·7	630·983	630·978
,, 33	Fe $K\alpha_1$	18·7	37 10 2·3	+0·3079	1 42·1	18 35 52·2	18 35 52·7	1932·055	
,, 34	,,	19·3	37 15 3·9	−0·6094	3 22·0	18 35 51·0	18 35 51·9	1932·077	1932·066

A relative measurement of one line with respect to another is so carried out that both lines are simultaneously exposed on the plate. Through measurement of the distance between the lines one can, knowing the length of the camera, easily calculate the angular distance.

Results of Measurements.

The work was so disposed that the lines Mo Kα_1, Mo Kβ_1, and Fe Kα_1 were determined through absolute measurements, as described in the foregoing. For molybdenum the line α_2 was measured relative to α_1, and β_2 and β_3 relative to β_1. For iron α_2 was measured relative to α_1. The results of the absolute measurements are assembled in Table I. The results of the relative measurements in the first and higher orders are collected in Tables II. and III. respectively.

TABLE II.

Relative measurements in first order.

Plate.	Line.	a (mm.).	$\Delta\phi$.	$\overline{\Delta\phi}$.	ϕ.	λ (X.U.).
S.L. 5...	Mo Kα_2	0·3053	2′ 25″5			
„ 7...	„	0·3066	2 26·1			
„ 9...	„	0·3061	2 25·9			
„ 15...	„	0·3043	2 25·1			
„ 19...	„	0·3064	2 26·0			
„ 29...	„	0·3085	2 27·0			
„ 37...	„	0·4424	2 26·7	2′ 26″0	6° 45′ 1″3	712·089
„ 22...	Mo Kβ_3	0·0437	20·8			
„ 23...	„	0·0426	20·3			
„ 32...	„	0·0430	20·5			
„ 39...	„	0·0633	20·9	20·6	5 59 3·1	631·579
„ 32...	Mo Kβ_2	0·8090	6 25·6			
„ 39...	„	1·1662	6 26·6	6 26·1	5 52 16·4	619·698
„ 33...	Fe Kα_2	0·4250	2 20·9	2 20·9	18 38 13·2	1935·987

TABLE III.

Relative measurements in higher orders.

Plate.	Line.	Order.	a (mm.).	$\Delta\phi$.	$\overline{\Delta\phi}$.	$\Delta\lambda$.	λ.
S.L. 24...	Mo Kα_2	2	0·6925	5′ 0″0			
„ 30...	„	2	0·6311	5 0·8	5′ 0″4	4·284	712·115
„ 26...	„	3	0·9806	7 47·4			
„ 28...	„	3	0·9794	7 47·6	7 47·5	4·285	712·116
„ 31...	Mo Kβ_3	3	0·1283	1 1·2	1 1·2	0·569	631·547

For the plates S.L. 33, 34, 37, and 39 the length of the camera is 622·11 mm., and for all the other plates the length s 432·76 mm.

Wherever relative measurements in higher orders than the first were made, $\Delta\lambda$ was calculated by the formula $\Delta\lambda = \frac{2d}{n}\cos\phi\,.\,\Delta\phi$. The value taken here for ϕ was the mean of the angles of reflexion for both components. In the final calculation of the mean wave-lengths the measurements in the first order were assigned weight 1, measurements of the second order weight 2, and measurements of the third order weight 3. This was motivated by the increased dispersion in the higher orders, and also by the fact that the molybdenum lines in the second and third orders are so sharp that the measurement of their distance can be made with almost as great accuracy as in the first order.

The definitive results of the wave-length measurements are collected in Table IV.

Table IV.

Definitive results ($d' = 3029{\cdot}04$ X.U. and $R = 109737$ cm.$^{-1}$).

Line.	λ (X.U.).	$\frac{\nu}{R}$	$\sqrt{\frac{\nu}{R}}$
Mo $K\alpha_2$	712·105	1279·692	35·7728
„ α_1	707·831	1287·420	35·8807
„ β_3	631·543	1442·935	37·9860
„ β_1	630·978	1444·227	38·0030
„ β_2	619·698	1470·515	38·3473
Fe $K\alpha_2$	1935·987	470·706	21·6958
„ α_1	1932·066	471·658	21·7177

Accuracy of Measurement.

The factors that chiefly determine the accuracy of measurement of the wave-lengths of X-rays are: the homogeneity of the rays, the properties of the crystal, the principle of measurement, the design and construction of the spectrograph, and the way in which the potentialities of the apparatus are turned to advantage.

The radiation in a given X-ray line is not fully homogeneous; the emitted radiation comprises a certain small

wave-length range which, for wave-lengths of the same order of magnitude, is minimum for the K-series and increases successively for the L- and M-series. For a given series, *e. g.* the K-series, the wave-length range usually increases upon increase of wave-length ; *i. e.*, when elements of lower atomic number are approached. Since it is conceivable that the energy of radiation is unsymmetrically distributed on opposite sides of the wave-length at which the intensity of radiation has its maximum (as the writer has observed for the $K\alpha_1$ line of iron, using this spectrograph with its high dispersive power), it follows that the results may vary somewhat, depending on the time of exposure. For molybdenum, on the other hand, the sharpness of the lines is very marked (the wave-length range about 0·08 X.U.), and the wave-lengths of these lines can therefore be very accurately determined. Figs. 7 and 8 (Pl. XVIII.) give an idea of the sharpness of the lines. For the $K\alpha_1$ line of iron the wave-length range is considerably larger, and therefore the wave-length cannot be measured with the same accuracy here as in the case of molybdenum.

Regarding the crystal's influence on the accuracy of measurement, it may be said that it should give as sharp lines as possible, and that the reflecting atomic planes should be as uniform as possible. In this respect the crystal used in the present work leaves nothing to be desired. As stated above, the sharpness of the lines for molybdenum was especially good. To test the uniformity of the crystal, the $K\alpha_1$ and β_1 lines of Mo were exposed simultaneously. The angle of reflexion determined from this test was $6^\circ\ 42'\ 36''{\cdot}5$ relative to β_1, while the absolutely determined angle was $6^\circ\ 42'\ 35''{\cdot}3$. The difference is thus only $1''{\cdot}2$, in spite of the fact that the areas on the crystal surface from which both lines were reflected lie at a distance of about 3 mm. from each other. This result shows that the distortion is extremely slight. Since in absolute determinations the angle 2Δ need not appreciably exceed $5'$, it is obvious that the part of the crystal that here comes into use is very small. The distance from the slit to the axis of rotation is about 25 mm., and thus for Mo $K\alpha_1$, with double exposure, the distance between the central lines of the two areas on the crystal that reflect these lines is only 0·3 mm. With a slit width of 0·02 mm. the breadth of the *reflecting* area on the crystal is 0·17 mm. The distance between the inner boundary lines of the two reflecting areas is thus only 0·13 mm.

Thus on account of (1) the great sharpness of lines in the molybdenum radiation, (2) the unmeasurable distortion of

the atomic planes, and (3) the fact that an extremely small part of the crystal is used, it may be regarded as established that the calcite crystal employed does not give rise to any errors that can in any way affect the results of measurement.

Professor Siegbahn has pointed out that the crystal may be so adjusted that in absolute determinations the two reflecting areas completely coincide. This is accomplished by displacing the crystal forwards or backwards through the distance $\frac{b \cdot \sin \Delta\phi}{\cos \phi}$ (b = distance from slit to axis of rotation), according as ϕ_0 is greater or less than ϕ. This circumstance thus renders possible the making of accurate measurements, even with less uniform crystals.

That the principle of the measurements is sound is testified to partly by the fact that eventual defects in the uniformity of the crystal are eliminated. Other important circumstances may be mentioned :—Through reversing the crystal and plate-holder the distance between the lines on the plate becomes so short that small irregularities on the surface of the plate cannot give rise to errors. As the angle $2\phi\Delta$ is of the order of magnitude 5′ or less, a given minor error in the distance from slit to plate causes only a very slight error in the angle of reflexion. If, with a camera length of 432 mm., the error in this length amounts to 0·04 mm., the error in the glancing-angle when measurements of molybdenum are made amounts to 0″·03, which may be regarded as the upper limit. Professor Siegbahn has developed a method for taking double exposures at higher wave-lengths by means of the vacuum spectrograph, using Bragg's focussing method. In this method the axis of rotation and the crystal surface must completely coincide in order that correct results may be obtained. This is not the case here, however, as the result of an error in this adjustment is merely that the distance between the two reflecting areas on the crystal surface assumes another value. A trial exposure with the crystal somewhat displaced gave the same angular value.

An important circumstance is that the penetration of the rays into the crystal does not involve any error, as the rays do not pass the slit before they have been reflected by the crystal.

The lateral adjustment of the slit is, to be sure, made with great care, but the result of an error in this connexion is only that the effective area of the crystal is displaced—the size is not increased. If the slit is not fully parallel to the axis of rotation, the lines will be somewhat inclined but still parallel. The maximum error on this account may

conceivably be of the order of magnitude 0″·001 at the most, and thus need not be considered.

On the other hand, it is important that the atomic planes be parallel to the axis of rotation, for otherwise the lines will not be parallel, and the result will be more uncertain. It may be remarked that when defective adjustment of the crystal in this connexion was made at the beginning of the experiment, the result was that the value of the angle of reflexion obtained from 13 exposures varied within two seconds. The mean value of these preliminary exposures, which were not included in the results of measurement, was, however, 6° 42′ 35″·4 ; consequently only 0″·1 greater than the value obtained in the definitive measurements.

By reason of geometric conditions the lines are somewhat curved. It is therefore important always to measure the distance between the lines at the point where this distance is least or greatest, according as the angle ϕ_0 is less or greater than ϕ. The result of the adjustment of the anticathode is that it is just at the height of the shadow of the cross-hairs that falls in the middle of the lines. Now arises the question of how great the error in the height of the anticathode may be, or through how great a range along the length of the lines it is permissible to carry out measurements of distance in order that the angular error may not exceed a certain value $d\phi$. We construct the equation for the curve built by one line on the plate, and then assume that the focus-spot consists of a horizontal line. In a rectangular coordinate system (xy) with the y-axis as a tangent to the curve we get, with some small approximations, the equation for the curve:

$$x = \frac{r \tan \phi}{2A^2} y^2.$$

The line may thus be regarded as a parabola. r is the length of the camera and A the distance of the plate from the focus-spot. For $a = 432$ mm. and $A = 500$ mm. we get for Mo $K\alpha_1$

$$x = 0{\cdot}000102\, y^2.$$

As the length of the line is 20 mm., the difference becomes 0·020 mm., provided the distance between the lines is measured at the cross-hairs or at one end of the lines. A control determination gave exactly this value.

In order that the error in the angle ϕ shall not exceed $d\phi$ seconds, the following condition must obtain:

$$y \leq 0{\cdot}0031\, A \sqrt{\frac{d\phi}{\tan \phi}}.$$

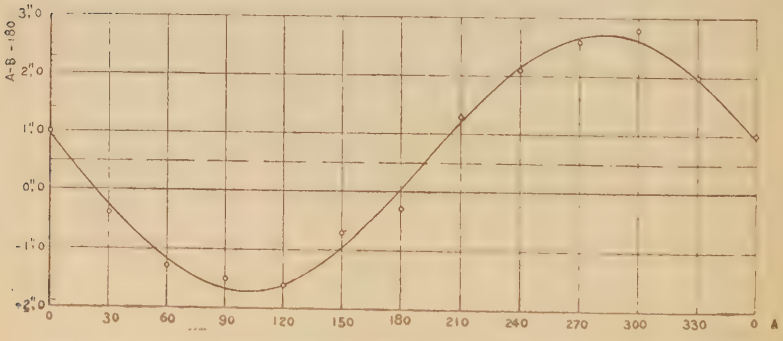
If $d\phi \leq 0''{\cdot}05$, we get for Mo $K\alpha_1$

$$y \leq 1{\cdot}0 \text{ mm.}$$

To prevent the occurrence of any significant error on account of the curvature of the lines, the measurement of the distance between the lines should be made within a region about 2 mm. in length, located with respect to the cross-hairs. No difficulties are encountered in placing the X-ray tube in such a *niveau* that the focus-spot falls inside this interval.

The quality of the circular scale is in a high degree determinative of the accuracy of measurement. It was tested in two different ways. One test was so carried out that adjustments were made at even 30° intervals. In every case the reading with the ocular micrometers was taken in the same way as in the absolute angle-determinations. The difference between the readings of microscopes A and B, decreased by 180°, was plotted as a function of the readings of microscope A (fig. 9). In this way the points of the

Fig. 9.



curve are experimentally determined. The curve is of sine form, and was adjusted to the points by the method of least squares. The differences between observed values and the curve, expressed in seconds, are:

A = 0°	= +0·04	A = 180°	= −0·34
30	−0·20	210	+0·10
60	0·14	240	−0·06
90	+0·17	270	0·07
120	0·00	300	+0·20
150	+0·27	330	+0·04

As has been seen, the values are very small and the differences between readings of the two microscopes are due

chiefly to a somewhat eccentric location of the scale. Since, however, the readings are taken with two diametrically-opposed microscopes, it is evident that the eccentricity cannot give rise to error in the angular measurements.

The other test of the scale was so carried out that the glancing-angle for the Mo $K\alpha_1$ line was determined at three different zero-positions of the crystal. These were symmetrically divided, therefore, at 120° to each other. Two plates were exposed in each position. When this test was made, the atomic planes were, to be sure, not parallel with the axis of rotation, for which reason the absolute values of the angles of reflexion were not fully correct. But as all the plates were measured at the same height, and the apparatus was otherwise undisturbed during these exposures, it is obvious that the variations in the angular value give an idea of the quality of the scale. The following angular values were obtained in the three different positions :—

6° 42′ 36″·25,
6° 42′ 36″·00,
6° 42′ 36″·05.

The results of these tests show that, when the readings are made as described above, it may be considered that the errors in the scale fall considerably below 1″.

An additional source of error lies in the screws of the ocular micrometers. This possibility of error is eliminated, however, by the method of reading employed. From the examples given of the determination of the glancing-angle, it will be seen that only a very small part of the glancing-angle is measured with the ocular micrometers. The angles measured with microscopes A and B were 1″·6 and 2″·3 respectively. When a 5′ interval on the scale was measured with either of the ocular micrometers, a deviation from 5′ of at the most 2″ was observed. From this it follows that, since only such small angles as 2″ are measured with the ocular micrometers, the error becomes exceedingly small.

On account of the symmetrical structure of the spectrograph, variations in temperature cannot cause errors in measurement unless different parts of the instrument are at different temperatures, and displacements of such a lack of uniformity in the temperature distribution take place between two consecutive readings of the scale. As there is no reason whatever for such an unequal temperature distribution, the above-mentioned source of error may be left out of consideration.

An important part of the determination of the angle is

the measuring of the distance between the lines. Examination of the screw of the comparator disclosed no systematic errors greater than the chance errors in reading. The accuracy of measurement depends on the sharpness of the lines. For the molybdenum lines the width of the lines is not much greater than the width of the slit, while the iron lines are considerably wider. For the molybdenum lines the error probably does not exceed 0·0005 mm., corresponding to 0″·12, and for the iron lines we may consider the greatest error to be 0·001 mm., corresponding to 0″·17 (greater camera length).

It is also conceivable that errors may arise from the fact that the screw of the comparator gives correct results only at a certain temperature. A rough calculation shows, however, that the error in the angle of reflexion on this account does not exceed 0″·02.

In order further to illustrate the accuracy of measurement, it may be stated that, in taking the exposures of molybdenum plates S.L. 19, 20, 27, and 29, a camera-tube having a length of 432·76 mm. was used. In taking plate S.L. 37, an entirely new tube, 622·11 mm. in length, was used, and all adjustments were therefore repeated, and another portion of the scale was used for this plate. In spite of the greatest possible variation in the taking of the measurements, the angular value obtained for this last plate deviated only 0″·15 from the mean of the first four determinations.

Comparison with earlier measurements.

TABLE V.

	α_2.	α_1.	β_3.	β_1.	β_2.
Duane & Patterson (1920)[1].	712·36	708·07	631·32		619·91
Overn (1921)[2]	713·34	708·94	632·62		627·01
Hatley (1924)[3]	...	708·057			
von Nardroff (1924)[4]...	...	...	631·323		
Leide (1925)[5]	712·08	707·80	631·63	631·24	619·69
Allison & Armstrong (1925)[6].	712·175	707·865	631·657	631·094	619·823
Present results	712·105	707·831	631·543	630·978	619·698

[1] Duane & Patterson, Bull. Nat. Res. Counc. vol. i. part 6, p. 393 (1920).
[2] O. B. Overn, Phys. Rev. xviii. p. 350 (1921).
[3] C. C. Hatley, Phys. Rev. xxiv. p. 486 (1924).
[4] R. von Nardroff, Phys. Rev. xxiv. p. 143 (1924).
[5] A. Leide, *Comp. Rend.* clxxx. p. 1203 (1925).
[6] S. K. Allison and A. H. Armstrong, Phys. Rev. xxvi. p. 701 (1925).

A calcite crystal was used in all these measurements, with the exception of Overn's, in which a rock-salt crystal was used ($p=2\cdot814$). The measurements of Duane and Patterson, Hatley, von Nardroff, and Allison and Armstrong were made with an ionization spectrometer, while Leide's measurements were made with a photographic spectrometer built on the same principle as that used by the writer.

The refraction of X-rays upon reflexion from a crystal has been studied experimentally by Stenström, Hjalmar, Bergen, Davis and his co-workers, and by the author *. The results of these studies show that the usual optical laws of refraction upon reflexion from a crystal are, in the first approximation, also applicable to X-rays. On account of this, Bragg's law of reflexion is to be slightly corrected. With a view to the refraction, the wave-length in air is to be calculated by the formula :

$$n\lambda = 2d\left(1-\frac{\delta}{\sin^2\phi}\right)\sin\phi,$$

where d is the lattice constant, ϕ is the observed angle of reflexion, and $\delta=1-\mu$, where μ is the index of refraction.

In view of the fact that in all the previous tables of wave-lengths no regard has been taken of the refraction, the lattice constant has in this work been so chosen that in the first order

$$d'=d\left(1-\frac{\delta}{\sin^2\phi}\right)=3029\cdot04 \text{ X.U.}$$

According to Lorentz's dispersion formula, which has been shown to be valid for the normal dispersion of the X-rays, we get

$$\delta=1\cdot85\,.\,10^{-6} \quad \text{and} \quad d=3039\cdot45.$$

Duane and Patterson have calculated the wave-length, using the value $d'=3028$ X.U. Leide, like the author, has used the value $d'=3029\cdot04$ X.U. Overn, who made use of a rock-salt crystal, has taken $d'=2814$ X.U. Hatley, von Nardroff, and Allison and Armstrong have corrected for the refraction and taken $d=3028$ X.U.

In order to compare all these measurements, the values of the wave-lengths obtained by the different investigators have been recalculated for $d=3029\cdot45$ (corresponding to $d'=3029\cdot04$) and $\delta=1\cdot85\,.\,10^{-6}$, and these new values are given in Table V.

Of greatest interest is the comparison between Leide's measurements, Allison and Armstrong's measurements, and the writer's. The amount of the deviations, expressed in angular measure, can easily be calculated, as a change in wave-length of 0·01 X.U. corresponds approximately to $0''\cdot34$.

* Axel Larsson, *Z.S. f. Phys.* xxxv. p. 401 (1926).

Allison and Armstrong, who used the ionization spectrometer, state that the error in the determination of the position of the intensity maximum alone may amount to 3″. Since, moreover, there must be considered other errors, such as errors in the scale and errors in reading the same, it is obvious that deviations from the writer's results amounting to at the most 4″ lie within the limits of error of the values obtained by Allison and Armstrong. All the angles determined by Allison and Armstrong were larger than those determined by the writer.

As to Leide's measurements, it is seen that the difference between his values and the writer's for the α_1 and α_2 lines is only 1″. For the β_3 and β_1 lines, on the other hand, the deviation is considerably greater. Leide's wave-length values for the β_1 lines, however, coincide with the mean of the writer's β_1 and β_3 lines. This indicates that this doublet in Leide's measurements, which were made in the first order, was not resolved into its components. The wave-length of the β_3 line he calculated by measuring the doublet distance in the third order and adding this value to the wave-length of the doublet $\beta_1\beta_3$. Because of this, the wave-lengths for β_1, as well as β_3, have become somewhat in error. The wave-length for β_2, on the other hand, was measured in the first order relative to the doublet $\beta_1\beta_3$, and therefore deviates but little from the writer's values. Leide's value for the doublet distance, $\beta_3-\beta_1=0{\cdot}72$ X.U., deviates from the values of Allison and Armstrong ($=0{\cdot}563$) and the writer ($0{\cdot}565$), which show surprisingly good mutual agreement. The frequency-difference measured by the writer is $1{\cdot}292$, and by Allison and Armstrong $1{\cdot}287$. The frequency-distance for Mo L($\beta_3-\beta_1$), measured by Coster in Siegbahn's laboratory, is $1{\cdot}28$. According to the atomic theory, these values should be identical. It is evident that the agreement is very good.

Apart from these lines, Leide has measured a very weak line, β_4, with the wave-length 618·8 X.U., thus with shorter wave-length than β_2. Allison and Armstrong have sought after the same line, but have not succeeded in finding it. The plates reproduced in this article show traces of what may possibly be a line with the above wave-length.

I take this opportunity to express to my teacher, Professor Manne Siegbahn, my heartiest thanks for his kindness in placing at my disposal the apparatus used in these investigations, and, above all, for his never-failing interest and goodwill.

Physical Institute, University of Upsala,
June 1926.

CXI. *Note on the Vibrational Movements which occur during the Inflammation of Combustible Gases.* *By* J. D. Morgan, *D.Sc.**

IT is well known that the movement of a flame through a combustible gas mixture is often accompanied by a vibratory motion of the flame front. Among recent workers Wheeler has shown by photographic investigations of explosions in glass tubes (open at one end, and ignition occurring at the open end) that, under favourable conditions, longitudinal vibratory movements of large amplitude are sometimes developed in the later stages of inflammation. The writer has shown that in the combustion of coal gas and air in tubes closed at both ends (ignition at one end) the pressure fluctuations accompanying the vibrational movements are, under favourable conditions, surprisingly large, pressure differences of 50 lb./sq. in. on the tube end due to vibrations only having been observed.

It is also well known in connexion with explosions occurring in metal tubes closed at both ends that the explosion of a gaseous charge of a given composition in one tube may be inaudible, whilst an explosion of a charge of the same composition in another tube of different length under similar initial conditions of temperature and pressure may be accompanied by a characteristic sound. There is considerable agreement of opinion that the audible effect sometimes heard is attributable to energetic vibrational movements of the gas.

Study of the vibrational movements occurring in gaseous explosions is of practical value in connexion with the phenomenon known as "pinking" in high-speed internal combustion engines. Pinking is the name given by engineers to that kind of explosion in an engine cylinder which is accompanied by an audible effect. When a normal explosion occurs in an engine cylinder no sound is heard, but in exceptional cases the explosion is accompanied by a sharp knock. There is good reason for believing that knocking, or pinking, in engines is the same phenomenon as that associated with explosions in closed tubes.

At the present time the development of petrol-engine designs is hampered by the fact that, when for a particular

* Communicated by Prof. E. Taylor Jones, D.Sc.

fuel the compression ratio exceeds a certain value, serious pinking occurs, and with this condition not only is there a risk of injury to the engine but the possibility of increasing the thermal efficiency is prevented.

The problem of knocking, or pinking, in engines has been studied hitherto mainly from each of two particular aspects. Engine designers—and in this connexion it is appropriate to mention the name of Ricardo—have recognized that the tendency to pinking found with a particular fuel, such as petrol and air, can be minimised by suitably shaping the combustion chamber and by placing the sparking plug at a suitable position. On the other hand, as is evidenced by the recent work of Callendar and his colleagues, and by the widespread interest evoked by the "anti-knock" properties of so-called "dopes," prominence has been given to the chemical reactions which occur during the process of combustion, and at the present time hope of a final solution of the pinking problem appears to be centred in the chemical studies which are being actively pursued.

The writer's experiments lead to the conclusion that pinking is due to a suitable correlation of two factors, namely, the rate of generation of heat in the flame front and the vibration frequency of the gas in the direction of travel of the flame *, these evidently being the significant factors in those two aspects of the problem to which attention has already been directed. To make clear the meaning of this statement a brief description will be given of certain experiments.

Two explosion vessels were used. Each was made from a steel tube of about two inches diameter. One tube was twelve inches long, and the other twenty-four inches. Both tubes were closed at each end. Ignition was effected at one end of the tube, and the rise of explosion pressure was recorded by means of a pressure indicator of the diaphragm type arranged at the opposite end. The indicator was designed to record not only the general rise and fall of pressure, but also vibrational variations of pressure. Movements of the indicator were recorded by the action of a spot of light on a photographic strip mounted on a revolving drum. Two sets of experiments were carried out with each tube. In the one a mixture of Birmingham coal gas (23 per cent.) and air was used, whilst in the other the mixture consisted of methane (8·5 per cent.) and air. The flame velocity

* "Some Experiments on Gas Explosions in Closed Tubes, with particular reference to Pinking," Journal of Inst. Automobile Eng., Dec. 1924.

in the coal-gas mixture was much more rapid than in the methane mixture.

In the methane experiments, using both the twelve and twenty-four inch tubes, the photographic records showed no sign of vibrational movements. A like result was obtained in the coal-gas experiments in the twelve-inch tube, but in the twenty-four inch tube the records showed strong vibrational movements. These were set up shortly after the initiation of the flame. At first the amplitude was small, and the frequency corresponded to that of sound-waves travelling through the cold or unburnt gas. With the continued movement of the flame the vibrations not only increased in amplitude but also in frequency. Later, harmonics were developed in the wave-motion. The vibrations reached the maximum both of amplitude and frequency at the completion of travel of the flame. Increase of frequency was due to the increase of temperature of the gas, and the harmonics were probably attributable to inequalities of temperature in the portions of the gas lying in front of and behind the flame. When the record showed vibrations, the explosion was accompanied by the characteristic sound above mentioned. Otherwise no sound was heard.

The experiments brought out the fact quite clearly that a gas which exploded without audible effect in one tube could develop pinking in a longer tube. This fact was confirmed later by Dr. W. A. Kirkby at Sheffield University. He found that pinking occurred when an 8·5 per cent. methane-air mixture was exploded in a tube rather more than six feet long. There was no sign of pinking with this mixture in the writer's two-foot tube. The experiments also brought out the further fact that in a given tube pinking can occur if the flame velocity, or, to use a more appropriate expression, the rate of heat generation, is sufficiently high. The study of these and other associated experiments therefore led to the conclusion that pinking was due to vibrational movement in the gas, and depended on a suitable correlation of the rate of heat generation and the vibration frequency of the gas in the direction of motion of the flame.

It is pertinent to inquire whether the relationship between the two factors on which pinking depends, in the conditions of the experiments cited, can be expressed in more definite terms. It is well known to engineers that there are degrees of pinking in internal combustion engines. Sometimes it is violent, and at other times it is barely perceptible. Only the violent kind of pinking is seriously harmful. The experiments already referred to showed that in the same explosion

apparatus gas mixtures of different proportions behaved differently, slowing-down of initial flame velocity being accompanied by reduction of vibrational movement. There can, however, be flame vibration without pinking. It would appear, therefore, that pinking is a matter of degree : the term is only applicable to conditions which are accompanied by strongly energetic vibrations, and there is probably no sharply defined transition from non-pinking to pinking conditions.

A useful model for assisting the study of vibrational movements similar to those set up in an air column consists of a helical spring which is suspended at its upper end from a rigid support, the lower end being free. It is convenient to make the spring from black enamelled wire, and to illuminate strongly one side of the spring. When in rapid motion the separate convolutions of the spring become invisible, but a light spot marks the position of each convolution, and the line described by the spot gives a visible indication of the distance through which the convolution moves. The series of bright lines along one side of the spring show how the amplitude of vibration varies along the spring. Taking hold of the free end and extending the spring slowly, no appreciable vibration is set up in the spring. But on moving the free end suddenly through a short distance, the extension of the spring is accompanied by a vibrational movement of each convolution which persists for a considerable time. The model enables the obvious facts to be clearly demonstrated, that visible vibration is only set up when the spring is extended at a sufficiently rapid rate, and the amplitude of vibration increases with the rate of extension. In other words, the model shows that vibration follows when the force is applied impulsively, the amplitude of vibration increasing with the suddenness of the impulse *.

* The writer is indebted to Prof. E. Taylor Jones for the following expression, which was given by the late Lord Rayleigh and may prove to be of value in the further study of vibrational motion in gases :

$$u = \frac{1}{n} \int_0^t \epsilon^{-\frac{1}{2}k(t-t')} \sin n(t-t') \mathrm{U}\, dt'.$$

It represents the displacement u at time t of an oscillatory system (frequency n, damping factor k) produced by a force U acting over the time from 0 to t'. If the total impulse $\int \mathrm{U}\, dt'$ is given, and if the damping factor k is small, the expression for u has its greatest value when t' is very small and t is such that $\sin n(t-t')$ is approximately equal to 1, that is, nearly a quarter period after the delivery of the impulse. The physical meaning is that under a given impulse an oscillatory system has the greatest possible amplitude of vibration set up in it when the impulse is delivered as suddenly as possible.

In the tube experiments above described it can be assumed that the flame front is at right angles to the axis of the tube and occupies the whole of the cross-sectional area of the tube interior. The flame travels from one closed end of the tube to the other. During the progress of the flame, heat is generated continuously by the combustion of the gas in contact with the flame front. But the rise of pressure following the combustion of a layer of gas in contact with the flame does not spread instantly throughout the tube. The burning of successive layers can be regarded as equivalent to applying successive pressure impulses to the gas. If the rate of generation of heat is slow, and the vibration frequency of the gas in the direction of motion of the flame is high, no appreciable vibration will be set up in the gas. With a slow rate of heat generation, an appropriate low-vibration frequency (in other words, a long tube) is necessary for the setting up of the vibratory condition. When the rate of heat generation is sufficiently high, vibrations will be set up in a gas having a high vibration frequency. For a given vibration frequency, the rate of heat generation necessary to cause vibration is not a fixed but a variable quantity which can probably be varied over a wide range, the amplitude of vibration being greatest when the rate of heat generation reaches the maximum.

There is an alternative way of considering the problem which may be of value, and that is of regarding it as analogous to that of the singing flame. In the familiar singing-flame experiment the flame is stationary in position, the tube (open at both ends) is vertical, and air is allowed to move through the tube. The characteristic feature is that more heat is given to the air in the tube during the compressions than during the rarefactions, and the amplitude of vibration gradually increases until the maximum is reached.

The conditions affecting the flame vibrations in a gaseous explosion are complicated by a variety of effects. For example, in the first place, whether the flame velocity is uniform or accelerated, the burning of successive layers of equal thickness will be accompanied by increasing rate of generation of heat, due to the increasing pressure and consequent increased density of the gas in the unburnt region. Also, the vibration frequency will increase due to increase of mean temperature, and the vibration frequency of the cold unburnt gas ahead of the flame will be different from that of the hot burnt gas behind the flame. Consequently, conditions which are not favourable to pinking at the commencement of the explosion may develop into favourable conditions during the course of the explosion. In some of

his experiments the writer found that the pressure rose gradually without sign of vibrational movement until the flame was near the end of its travel, and then a violent vibratory condition was set up suddenly. Explosions of this kind were usually among the most noisy.

If it is a fact that pinking results when rate of heat generation and vibration frequency are favourably associated, it follows that the tendency to pinking can be reduced by reducing the rate of heat generation, and this apparently is the objective of those working on the chemical side of the problem. But it is necessary to keep in view the complementary condition that by a change of engine cylinder size or design, or of the igniting position, it may be possible to neutralize the benefit obtainable from the lower rate of heat generation.

CXII. *Dielectric Attraction in Electric Fields.*

By G. L. Addenbrooke *.

[Plate XIX.]

Attraction of Liquids.

Preliminary.

In an account of Maxwell's work in the Cavendish Laboratory it is stated that, not long before his death in 1879, an experiment it pleased him to show visitors was to bring over a bowl of petroleum a charged metal sphere. The petroleum then rose up slightly and the surface became convex. Maxwell's attention was probably directed to dielectric attraction by Boltzmann's work in 1873 on solids, though the fact that dielectrics are attracted to electrical fields is alluded to in a few lines in De La Rive's work published in 1854.

My own first acquaintance with the phenomena met with was in 1897, when the late Sir Joseph Swan showed me the experiment described below on a viscous mixture of rosin and rosin oil, for which I lent him a Wimshurst machine. This, and other experiments, he afterwards embodied in a paper (Proc. Roy. Soc. 10th Sept. 1897) :—

"With a metal ball of 150 mm. diameter, 6 mm. above the surface of the liquid, and a proportionately larger disc, basin, and depth of liquid, acted upon by a machine of

* Communicated by the Author.

moderate power, the spark-gap being adjusted so as to prevent sparks passing from the ball to the liquid, and the tension such as to keep up a strength of electrification of the surface only slightly less than that which would cause disruptive discharges to pass, a column of liquid rises and connects the overhanging ball and the surface of the liquid in a manner strongly suggestive of water-spout phenomena. The ascent of the column of liquid is followed by the descent of numerous thin surrounding streams, and these keep up a regular system of upward and downward circulation."

Swan also describes the corresponding phenomena he found with an induction-coil field, but devotes his paper specially to the stress figures he produced on rosin surfaces, with this field.

That the above experiments might be developed struck the writer at the time and was emphasized when in two communications to the Phil. Mag. (May 1924 and Jan. 1926) he showed that the connexions between dielectric and other physical properties are much closer if the latter are compared with the mechanical pulls on dielectrics in electrical fields, than with the capacity or the energy stored due to these pulls.

General Observations.

Quantitive knowledge of dielectric actions has in the past been obtained from measurements on condensers and on the attraction between flat plates.

But these are simply the limiting case in one direction. The field being even there are two equal attractions in opposite directions. Both in nature and in engineering the fields are almost universally convergent or divergent, when there is also a mass attraction towards the strongest field.

There are, however, nearly always present further actions, usually referred to as "absorption" in steady fields, and dielectric hysteresis is alternating.

Nature of Absorption in Dielectrics.

The first quantitive experiments published on absorption were made by Fleeming Jenkin in 1860. In the course of the Board of Trade inquiry into the position of the submarine cable industry at that date, he was asked to what he attributed the effects. His reply was substantially that he could not decide whether they were an action on the dielectric itself, or on something diffused in it.

In his 1864 paper, when promulgating his heterogeneous theory of absorption, Maxwell quotes Fleeming Jenkin's work, though the reference is omitted in his book published in 1873. Since then scientific opinion has varied round these alternatives.

The second factor, namely "dielectric hysteresis," was not known until methods of measuring the effective energy of alternating currents—in addition to the voltage and current—were devised about 1895–7. The losses then found were at first attributed to a similar action to hysteresis in iron. Experience has not, however, borne out this view.

In previous communications to this Journal, Mar. 1922 and Mar. 1923 (also to 'Nature,' April 5, 1924), the writer has referred to work on this subject, and it will now suffice to mention what has occurred in the high-tension cable industry.

Twelve years ago cables having insulation of dried paper and mineral oil with other compounds had ordinary specific insulating resistances of certain values, and dielectric losses at 50 ~ approximating 2 per cent. of the charging energy. It was then found that for insulation to stand higher potential slopes the dielectric losses must be less. In the best cables the alternating losses have now been reduced to $\frac{1}{2}$ of 1 per cent., or to $\frac{1}{4}$ of those formerly general. At the same time, the specific resistance has been greatly increased.

These striking results are almost entirely due to the use of more perfect methods of drying. Intensive drying thus reduces so largely both dielectric conductivity and the so-called hysteresis, as to show that both depend on the presence of moisture. Laboratory experiments also lead to the view that a perfectly pure and dry homogeneous dielectric would have a sensibly "infinite resistance," and no absorption or appreciable losses in alternating fields as well as a constant capacity at varied frequencies.

High vacua work has also in the last few years shown that materials, including glass, occlude moisture. The probability is therefore suggested even here of absorption being due to the same cause.

Percentages of Moisture Present.

Paper ordinarily holds about 8 per cent. of moisture. The specific resistance is then of the order of 10^{8-9} megohms per cubic cm. In an alternating field of 50 ~ the power factor will be of the order of 20 per cent. A couple of thin sheets will usually stand an alternating voltage of 1000 under these conditions. With a little trouble in an alternating field, such paper can be dried electrically, the resistance

vastly increased and the power factor reduced to such figures as those quoted above. There is experimental evidence that when the power factor is reduced to $\frac{1}{2}$ of 1 per cent., the remaining moisture present is probably of the order of 1 part in 1000. Possibly it varies in its effects with the dielectric constant of the occluding dielectric, but this is still obscure.

Again, a thick mineral oil was taken, its conductivity and losses in an alternating field were measured. It was then heated to 185° C., and the moisture given off collected and weighed. It amounted to about 1/2000th part. Similar electrical measurements were then again made on the dried oil. The conductivity had decreased 26 times, and the losses in the alternating field by about 1/3rd. What moisture was still left it is difficult to say, the subject needs further investigation.

It is, however, amply proved that small fractions of 1 per cent. of occluded moisture give rise in dielectrics to important effects in electric fields. Experiment also leads to the view that a given percentage of moisture occluded in liquids has a larger effect than in solids. It is worthy of note that a dielectric occluding 1/1000th part of moisture has as many water molecules in it as the same volume of steam at nearly 2 atmospheres pressure.

Capacity Effects due to Absorption.

Again, if tests are made with the electrostatic wattmeter, or by bridge methods at varying frequencies, and especially at low ones, say 8–10 per sec.: when moisture is present, the capacity or purely reversible energy is greater the lower the frequency, and also is reduced in itself and its variability with frequency is reduced if moisture is extracted. With the highest extraction of moisture possible the capacity reaches a minimum and no longer varies sensibly with change of frequency. The temperature coefficient both of the losses in alternating fields and absorption capacity also decreases very markedly as the moisture is reduced, though that of the steady field resistance does not.

If the capacity of dielectrics containing small percentages of moisture is compared at low frequencies with that after a further known reduction in the moisture present has been made, the change in capacity is insufficiently accounted for on the basis that the water has a dielectric constant of 80. Apparently it must be broken up into ions, at any rate partly, these ions being sufficiently far apart to act as practically free opposite charges.

Action in Even Fields when Absorption is Present.

In even fields the molecules of a pure dry dielectric itself will simply be equally strained towards each electrode and there will be no tendency to mass movement.

If, however, contained ions are opposite free charges, there will be a pull on the + ions by the − electrode, and a similar pull on the − ions by the + electrode.

Ions of both signs will therefore tend to move outwards. If there is resistance to their passing through the surfaces of the dielectric, ions of opposite sign to the electrodes will tend to accumulate beneath these. As ions of the same sign repel each other, their increasing aggregation under the surfaces will slow down the rate of aggregation and the intensity of the action, as is found with absorption in steady fields. The resistance the ions meet with in passing through the dielectric will cause a dissipation of energy, which apparently is that measured as "electrical resistance" and "dielectric hysteresis" in alternating fields.

On any ions diffused in the dielectric there will be a directional pull depending on the intensity of the field. On the atoms forming the mass of the dielectric, on the contrary, there will be no directional pull, but only two equal and opposite strains.

The effects of an even field are, therefore, different on the atoms of the mass of a dielectric to those on ions diffused in it.

The movement of the opposite ions towards the two surfaces will occlude energy and thus increase the capacity.

Action in Divergent Fields when Absorption is Present.

In these fields, the most general case, there will be directional attraction both on the atoms of the mass of the dielectric and on ions diffused amongst them. But while the pulls on the atoms of the mass of the dielectric will depend on the rate of change of the potential slope at any point, the pull on the ions as single charges will depend on the potential slope itself as with an even field.

Consider a charged sphere above a dielectric with plane surface. The field will be strongest where the normal from the surface passes through the centre of the sphere. Here there will be the strongest pulls on ions in the dielectric with opposite charges, but the field being even here the pulls on the atoms of the dielectric will be equal in both directions.

On passing from the centre, however, the rate of change

of the potential slope increases, though the intensity or potential slope diminishes, slightly at first, but more rapidly as the angle increases. Thus while the attraction on diffused ions diminishes, the pull on the atoms of the dielectric increases up to a certain point where the reduction in the intensity of the field more than counteracts its increasing divergence. From this point or angle outwards the pull on the atoms of the dielectric decreases. The attraction on the ions decreasing from the centre of action.

Experimental Results considered on the above Theory.

Some two years ago work was begun on the lines of Swan's experiment quoted above to see how far evidence for or against the above views could be obtained with solid and liquid dielectrics. It will be seen from what follows that the evidence appears to support them.

Production of the Field.

For the above experiment with steady fields Sir Joseph Swan used a Wimshurst machine of mine which gave a 6 in. spark between terminals. As dielectric he used rosin oil. A smaller machine having two 8 in. plates and giving a spark of an inch of air will show the effects well. With this, and using a spherical electrode 15 mm. in diameter instead of 150 mm., the effects described below can be reproduced. Description alone gives only a general idea of the phenomena, experiment is essential for their proper appreciation.

Preliminary Experiments.

Swan's experiments were repeated and extended to a number of other dielectric liquids. All these showed confused actions of the same general character. It was also soon apparent that minute hairs or other impurities exercised a powerful influence.

Employment of very clean vessels and filtration of the liquids were thus indicated. The effects, however, still remained very complicated. There were confused risings of the liquids accompanied by hollows and often whirling motions.

What effect surface or occluded moisture might have then suggested itself. Each of the various liquids used was, therefore, specially dried by chemical means or heat, and similar experiments again made, using freshly poured out liquid in clean vessels, also previously dried.

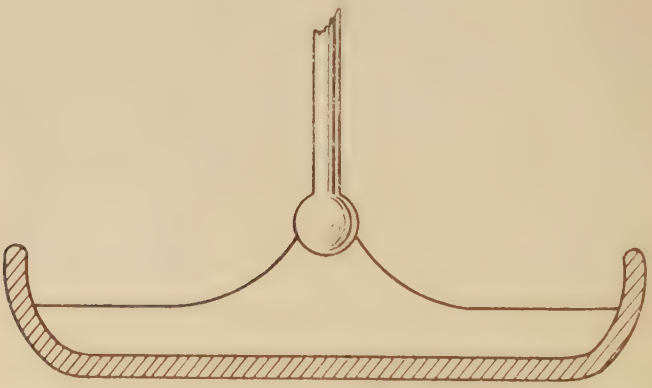
This procedure completely transformed the effects obtained.

Action with Pure Dried Dielectric Liquids.

One of the conductors from the source of potential difference ending in a sphere of about 1·5 centimetres diameter, being brought over the clean and dried liquid held in a clean and dried receptacle, the other conductor is earthed. The P.D. is next gently raised, avoiding sparking either to the liquid or across the air near it. The only action which now remains is that with the sphere at a distance of 5 to 6 mm. above the liquid,—with the field used in these experiments—the liquid quietly rises up, attaches itself to the lower part of the sphere, and remains firmly attached as long as the field is maintained.

The effect is shown approximately in fig. 1. It takes place with castor oil, the mineral oils, turpentine, in fact with all the highly dried and pure dielectric liquids experimented on up to the present.

Fig. 1.



The action is substantially the same whichever pole of the machine is used; indeed, if a large enough liquid surface is provided, and spheres connected to the two poles of the machine are brought over the liquid at some distance from each other, the liquid will on exciting the field rise up and embrace the lower parts of both spheres simultaneously, and will remain so attached to them as long as the field is maintained.

Through the kindness of the Cambridge Instrument Company I have been able to examine the effects with several of the above dried liquids with an alternating field of 12,000 to 15,000 volts 50 periods. They are as above described. Dry liquid dielectrics rise and maintain contact with the

electrode substantially as with steady fields. These and some other effects were also shown with the lantern at the late Exhibition of the Physical Society by the Henley Telegraph Company.

The only conclusion seems to be that the fundamental pull or attractional effect of a *divergent field* on pure and dry dielectric liquids has been isolated.

Action with Flat Electrode and Dried Dielectrics.

For the spherical electrode substitute a disk 5 cm. or more in diameter. With dried liquids the uplift now takes place near the edge of the disk and tends to spread round it. There is little or no uplift near the centre though the field is strongest there. The two pulls must therefore be equal and opposite.

At the edges the stresses will be weaker as the lines of force can spread out sideways. Opposite stresses will still exist though less intense. On the other hand, as here more lines enter a given volume of dielectric than leave it, there will be an additional component of the stress which pulls the atoms as wholes towards the strongest part of the field.

Thus, using a dried liquid dielectric, by a single experiment the fundamental actions in divergent and even electric fields can be visually demonstrated.

The similarity of the behaviour of the dielectric under these two different conditions to that of fine iron filings in equivalent magnetic fields is also manifest.

Effects with Undried Dielectrics.

The way is now cleared for investigating liquids which have not been specially dried.

Most dielectric liquids can be dried sufficiently by placing a number of fragments of calcium carbide, or calcined copper sulphate, in a bottle with the liquid. The bottle should then be left to stand for a day or two—being shaken at intervals. The dried liquid can now be mixed with varying proportions of the same liquid undried, and a series of samples obtained with different percentages of moisture.

If now the dried sample is taken and a small amount of the same liquid, but containing moisture, is mixed with it, and the above experiment is repeated, the column of liquid in the electric field will not be so quiet, little streams of liquid will be seen coming from the edges in contact with the spherical electrode and there will be more movement generally. Apparently, some of the moisture in the liquid

is broken up into ions where the field is strongest close to the electrode, and those of opposite polarity to the field are repelled, and having an attraction for the surrounding liquid carry a certain number of its molecules along with them.

If the same experiment is tried, but with a larger proportion of the undried liquid, the above effects will be more pronounced and there may be difficulty in getting the column of liquid to maintain full contact with the electrode, also there will be considerable tendency to form depressions.

Finally, if the experiment is tried with a dielectric having sufficient moisture, a regular maelstrom is often produced: protuberances rise up to the electrode, but are unable to maintain themselves; at the same time deep depressions are formed in other places, whirling motions are set up, and there is a constant change and confusion. All the effects may, however, be referred to the two causes already assigned:—the fundamental lifting action or pull, and the repulsion of ions of the same sign derived from the air, or from surface moisture or moisture in the dielectric. If there is an excess of ions of the same sign as the electrode at any point, repulsion will overcome the mass attraction and a hollow will be formed. Where, however, the liquid at any moment is comparatively free from these opposite ions the fundamental attraction will cause the liquid to rise, but the conditions being unstable there is constant change. It is impossible to convey any idea of these confused movements by a diagram.

To conclude the experiment, take this very same liquid, and dry it for a day or two. Then on putting it in the field as before, all these maelstrom effects will have vanished and only the quiet uplift of the dielectric into permanent contact with the electrode will remain.

It does not seem that better proof could be found that these repulsion effects are due to the presence of small percentages of ionized moisture in liquid dielectrics in their ordinary state, and that the fundamental mass action is a simple attraction.

Alternating Fields.—There has not been time to investigate fully what occurs in alternating fields under the above conditions, but some experiments have been tried in the Henley Telegraph Company's Laboratory which indicate considerable differences in the effects produced when moisture is present. The simple uplift appears to be much more persistent. This might be expected as there is less time for the opposite ions to aggregate, consequently their action will be more directly added to the action of the field on the mass

of the atoms of the dielectric. The action under these conditions should repay further investigation, especially if the experiments could be made over a range of frequencies going down to low frequencies.

Effects with Insulated Electrode.

A glass tube with bulb of the same size as the metal electrode was filled with mercury, and the latter connected to the source of Potential Difference. Contact between the metal electrode and the atmosphere is thus prevented and also with the liquid under experiment. Anything but purely inductive action is now excluded. The uplift is the same as before in all cases under the same conditions otherwise. The only difference is—that there being a less ready means of forming ions, the uplift is quieter with liquids containing moisture than when the metal of the electrode is exposed.

If, however, the liquid has once risen into contact with the glass bulb, a thin exposed film of liquid is left on it and either ions existing in this are separated, or moisture is occluded from the atmosphere on the exposed liquid surface. Ions are expelled from this and the tendency to oppose the uplift is increased.

Further Consideration of Repulsive Actions.

The above experiments with spherical electrodes have been extended over a number of dielectrics of different composition. All show the same characteristics with minor variations, and point to the conclusion that the repulsions found are due to the presence of opposite ions, and since these repulsions are absent when the dielectrics are thoroughly dried and pure, it would appear that these ions cannot be formed by breaking up of atoms or molecules of the mass of the dielectric, but must arise from the moisture occluded in it, or possibly on its surface.

Another possible source of ions must be considered in this connexion. In the neighbourhood of high tension conductors the atmosphere itself, or moisture in it, is liable to become ionized, and while the opposite ions will be attracted to the conductor, those of the same sign will be repelled and would be attracted to any near dielectric surface. When first making the above experiments with spherical electrodes it seemed that ions so formed probably had a large share in the repulsions found, but the above considerations and further experiments—which will be described later—do not support this view unless the electrode

is a point. With spherical electrodes ions formed from the surrounding atmosphere, while not altogether absent, seem to play an altogether subsidiary part in the phenemena found.

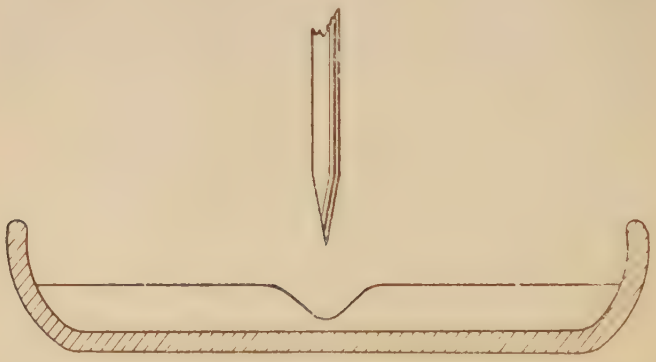
Effect with Point Electrode and Steady Field.

First perform the experiment as above described on a pure dry liquid and get it to rise up smoothly and hold on to the conducting sphere. Then keeping everything else the same, substitute a point for the sphere on the end of the conductor over the liquid.

On applying the P.D., instead of the dried liquid dielectric rising smoothly up and attaching itself firmly to the conducting sphere, there will be produced a conical hollow in the liquid under the conducting point, that is: the effect is exactly the reverse to that produced before.

The action is as if a fine jet or air were being blown

Fig. 2.



vertically down on the liquid forming a deep and well-defined depression in it as roughly shown in the illustration (fig. 2).

The action is substantially the same with fields of both signs on the electrode, but with a − field the effect is decidedly smaller.

On careful observation it will also be seen that if the field is maintained there is a constant circulation of the liquid from the outside of the hollow towards the edges.

Although the most manifest action is the production of this hollow, if the edges of the liquid are watched when the field is put on it will be noticed that the edges fall, which shows there is some uplift towards the centre, though it is not easily seen. Again, it will be found that there is often a ridge in the moving liquid as it approaches the edge of the

basin rising towards the outside. Apparently opposite ions from the edges are attracted to this distance to meet ions flowing out from the centre where their charges will neutralize. These latter actions are also substantially the same with either sign of field, but the circulation of the liquid is more pronounced with a positive electrode.

If the opposite electrode of the machine is insulated the effect is still produced. Under these conditions if a conductor is brought near the opposite electrode, a spark passes, and if at the same instant the surface is watched, signs of instantaneous striation round the hollow can be often seen. This effect, while not easy to reproduce, is obtained much more definitely by the following procedure. The above effects are also found with alternating fields.

Effects with Point Electrode using Induction Coil for producing the Field.

A coil giving a good discharge at 2·5 cm. shows the effects well.

First, the pointed electrode with this coil is fixed at about 2 cm. above the dielectric liquid. The effects to be described are found with several different liquids, but they can be most easily followed with oils of considerable viscosity such as a fairly heavy mineral oil. The surface must be viewed by strong reflected light. A spark gap is inserted in the circuit to nullify the make potential.

Action with Positive Electrode.—On starting the coil hardly any general disturbance occurs, but over a considerable area of the surface small splashes will be seen. The direction of these splashes is from the centre outwards, but the area under the centre is not specially disturbed. As the result of numerous experiments under varied conditions the only conclusion seems to be that these splashes are due to the action of definite charges.

One view which suggests itself is that ions are formed near the point by breaking up molecules of the air or of moisture in it, due to the intensity and rapid variation of the field. Ions of opposite sign would then be attracted to the point and those of the same sign violently repelled, and being attracted to the dielectric surface, which is also oppositely electrified inductively, fall on it. Then self-repulsion and attraction for the opposite electrification of the edges of the vessel cause them to shoot outwards; also their attraction for the mass of the dielectric and towards the bottom of the basin, causes them to sink dragging molecules of the dielectric with them producing indented

splashes of the forms indicated in the accompanying photograph (Plate XIX. *a*). The splashes look like slight grooves cut in the surface.

These splashes must, apparently, be due to a number of ions, as there are often two or more rays starting from a centre, a fact which is not easily accounted for on the above view. Again, opposite ions may be drawn out of weak points of the surface, leaving an excess of ions of the same sign, which then explosively repel each other. An hypothesis of this kind seems to fit the phenomena best, but further experiment is needed to get at the origin of what occurs with certainty.

The splashes can be produced with a steady field, but not so easily or in such numbers as with the induction coil.

While the general effects are the same there are minor differences as the conditions are varied. For instance, the splashes are deeper if the layer of liquid above the minus electrode is thin. Again, if the liquid is contained in a metal vessel about 7 cm. diameter, the splashes are elongated and extend very rapidly to the edges, and there is more symmetry and radial pattern Whereas, if the dish is larger and the liquid deeper the splashes are more promiscuously arranged.

By using a glass dish with a metal rim and placing a transparent dielectric in it, say castor oil, it is possible to follow the shapes of the splashes. Place a white surface under the dish and the whole in sunlight, or under a powerful parallel beam of artificial light. The splashes appear as dark sharply defined shadows on the white surface. By using a lantern with double reflexion and a glass-bottomed vessel the action can be thrown on a screen. The splashes now show as bright spots or lines.

Many of these splashes are of V-shape or have two or more tracks starting from a common centre, the point of origin being towards the centre. The rays are all of the same general character, but more elongated as the ions fall nearer the centre, as here the mutual repulsions are stronger and presumably the ions travel further radially along the surface of the dielectric, and before coming to rest.

Owing to the intermittence of the coil, the uplift on the mass of the dielectric is much less than with a steady field. At the distance of the electrode mentioned above no uplift is visible.

If the experiment is made in the dark, a diffused brush or corona starts from the electrode and covers the dielectric surface : this brush inclines to take the form of streamers.

If, after the liquid surface has been bombarded for some time, an insulated proof plane is brought close down over it and touched by the finger, on approaching the plane to a charged delicate electroscope it shows that the liquid surface has a charge of the same sign as the electrode which gave rise to it.

There are other details in the actions which would necessitate more space to describe, and surface moisture seems to play some part.

Effects with Negative Electrode.—Similar effects are produced, but the area bombarded is smaller as are also the sizes of the splashes : the pointed electrode must also be brought proportionately nearer the liquid surface.

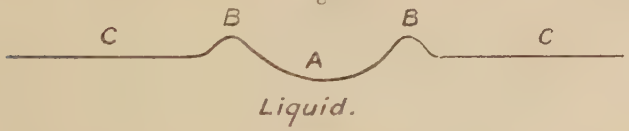
The effects in both cases are very striking and must be seen to be properly appreciated.

Effects with Pointed Electrode nearer the Dielectric.

Under the same conditions ; otherwise bring the point from 2 cm. distance from the dielectric surface to $\frac{1}{2}$ cm.

The area covered by the splashes is reduced and they are much more numerous. Now, however, a new phenomenon makes its appearance. Instead of the centre being com-

Fig. 3.



paratively inactive, it becomes the seat of intense action. There is a slight depression, on the surface of which a grooved star forms, the outer edges being slightly raised. Beyond this the splashes occur as before. (See Plate XIX. *b* for negative effect.)

Apparently now the stronger field acts directly on moisture in the dielectric, decomposing it, attracting opposite ions, and leaving ions of the same sign as the electrode on the surface. These then violently repel each other and are projected radially outwards.

If the effect is produced on rosin oil, which is very viscous, the surface takes the form shown in fig. 3. A is a circular hollow, B a circular ridge which stands up prominently over the surface of C ; indented rays start out of the ridge shown at B, their direction being radial from a centre at A.

In this shooting out of the rays over the surface, surface moisture plays a part—as will be described later. With a very viscous dielectric it can be seen that the rays shoot over the surface first and indent themselves afterwards.

Action with Negative Electrode.—The action is substantially the same as with the positive electrode, but on a smaller scale.

Effects with Insulated Point.

An electrode was used formed of a glass tube drawn down to a fine point. The tube was then filled with mercury. The point had to be brought rather nearer the liquid, but the formation of splashes was not sensibly different to when an exposed metal electrode was used. It would therefore appear that the splashes on the surface of the liquid cannot be due to anything thrown off from the metal electrode.

Effects with Thin Long Wire placed over and parallel to Surface of Liquid.

Using an induction coil to produce the field as above, similar effects to those described are produced when a straight wire is stretched horizontally above the surface of the liquid. The splashes now occur along the whole length of liquid under the wire.

We have thus a mechanical effect produced by the corona discharge showing how energy is dissipated. It is very observable how the effects are intensified under any slight downward bends or irregularities in the wire.

Action with Spherical Electrode and Induction Coil.

On substituting a sphere at a short distance above the liquid for the point, the actions described are modified. Any tendency to form ions from the atmosphere is decreased, but the direct pull on opposite ions on the surface, or in the dielectric, is increased and occurs over a larger surface.

This leaves a larger area of ions of the same sign under the electrode; the self-repulsion is stronger and seems to attain free explosive force; on starting the induction coil, rays shoot out radially from the outside of the central area and spread considerable distances over the dielectric surfaces in star forms. The kind of the effects produced are shown in the photos *c* and *d* (Plate XIX.), *c* being + and *d* −.

The distance the rays shoot across the surface depends on the film of moisture on it, as the following experiment shows. A shallow metal dish was filled with rosin oil and placed on

a metal platform mounted on the metal receiver-plate of an air-pump. Over the whole a bell-jar was placed. The upper opening of the jar was filled with a paraffin stopper through the centre of which a metal rod passed having a sphere attached to the end. The rod was adjustable. The field was connected to the rod and the other electrode to the receiver-plate.

The above effect was then obtained and the distance the rays shot over the surface was noted.

A bowl of calcium chloride was next placed under the jar. As the air became drier the effects produced were noted from time to time. While if anything more definite and clear, the star formed by the field became gradually less in diameter until at the end of a week, with the same field, the rays were of only half the radius found with the undried dielectric.

These effects are similar to the stress figures which Swan discovered. He afterwards produced them in a modified way, viz.: by coating plates with melted rosin about 1·5 mm. thick, and sparking on to the plate when cold. If the rosin was then warmed, the figure appeared on the surface and the rays sank into the material, becoming indented. He found that 24 hours could elapse between the production of the figure and its development by heat without altering its character. In fact, he found that if a charge was given to a rosin surface signs of it were apparent for two months afterwards. I have repeated and verified this.

The significance of these stress figures has been overlooked. Swan worked out a very delicate dusting process with sulphur and red lead by which the charges on the surface were shown, and his paper is illustrated by beautiful photographs of these. They are a more scientific form of Lichtenberg's figures, and have apparently been looked on as merely a variety of them. But work by the writer shows that such figures are the result of a dual action. After being shot out, as described above, the ions then react with the surface moisture between the rays, and it is this reaction that apparently gives rise to the fern-like growths which characterize Lichtenberg's figures, and on which attention has been concentrated. These are chiefly, however, surface effects; behind them lie the more fundamental actions which, evidently, precede the action which causes the fern effect.

Observation with a continuous field gradually brought up to full strength shows that these rays are suddenly shot out at a certain stage with explosive force over the surface; but

the effect is less easily produced with a steady field than with an induction coil.

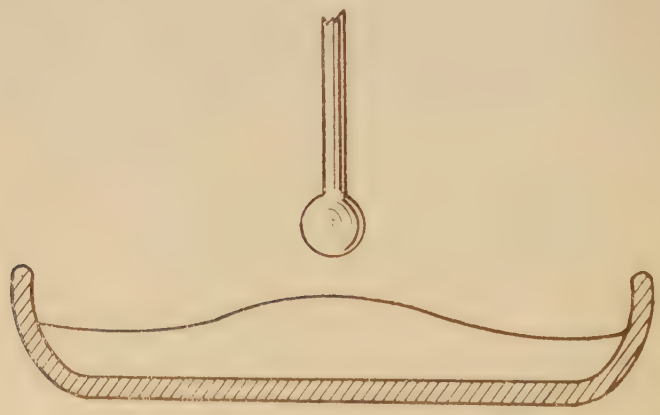
If a very viscous dielectric is employed the star is hardly visible at first, but quickly sinks until it forms quite deep indentations. Evidently there are strong charges repelled by the field and attracted to the mass of the dielectric and to the oppositely charged under surface of the containing vessel.

Apparently these charges must lie finally beneath the surface. Having regard to the conductivity of surface moisture it hardly looks as if they could remain on it any length of time.

Action of Divergent Electric Fields on Water itself.

With a steady field and the electrode some distance above the surface, water rises in a convex form, as in fig. 4, and as it does with dielectrics generally.

Fig. 4.



When the electrode is brought nearer the surface, or is more strongly excited, the dome rises higher. The liquid then alters its form to a pyramid which jumps up and down very rapidly. Examined in darkness, a thin line of visible discharge momentarily connects the electrode with the apex of the cone.

The contour varies approximately between that of the higher line in fig. 5 just before discharging, and the lower line after each discharge. The oscillation is very rapid.

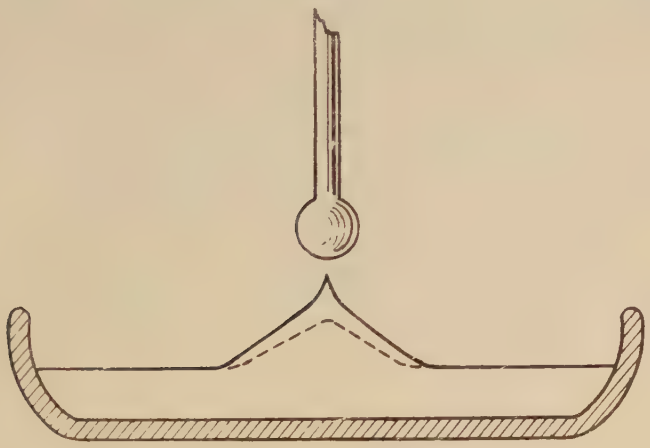
If the K of water is taken as 80, the pull on it would be nearly equal to that on similarly shaped metal. But if my

views are correct, by far the greater part of this dielectric constant is due to the presence of opposite ions in the water.

When the field is established, the action is on both forms of capacity and causes first the dome-shaped uplift, but if maintained, opposite ions aggregate more densely at the point of greatest potential slope, and the pull is stronger than over the rest of the area. This causes the contour of the liquid to change to a pyramidal form.

So far the aggregated opposite ions are restrained from breaking through the surface apparently by the surface tension, but finally they do so at a very fine point, there is

Fig. 5



a discharge, the attraction is momentarily lessened, and the cone sinks.

The oscillation and its frequency depend on the state of the water surface. They are greatest when the water is distilled and the surface clean : if the water stands with the surface exposed, impurities settle on it when the oscillation is less and the cone is not drawn up so high.

So far these water cones have been described as of pyramidal shape ; the sides are, however, concave when the cone is at its highest.

If what is said above as to the attraction is correct, water should be drawn up higher than ordinary dielectric liquids in equal electric fields ; but the apex of the cone begins to discharge before the attraction has time to exert its maximum effect.

The fact that there is so much of what is called "conductivity" in water as compared with that in good dielectrics, seems to account for the field producing general and not localized effects.

Addition of Salts to Water.

If salts are added to the water the effects are only slightly altered, presumably because there are already enough ions in pure water to raise its fundamental attraction to within 3 per cent. of that for a metal.

Induction Coil Field.—With this form of field little visible effect is produced either with pure water or when salts are dissolved in it, a simple line of sparks passes between the surface and the electrode; owing to the intermittence there is only a slight lifting effect.

Conclusion.

The above experiments illustrate, visually, the action of divergent electric fields on liquid non-metallic matter. Divergent fields are almost universal both in engineering and in nature.

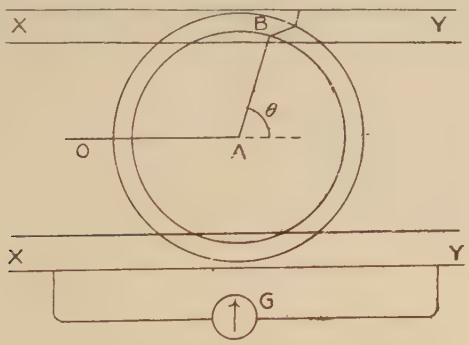
It has only been possible to describe what occurs to a first approximation, and very imperfectly. To appreciate the amount of definite detail the experiments themselves must be seen, since beyond the general effects there are, with variation of the conditions and of the liquid, numerous smaller differences which repay examination.

I have to thank the Henley Telegraph Company for working out effective means of demonstrating the attractive and repulsive effects in the lantern. Also Dr. D. Owen for demonstrating the possibility of showing the surface effects in the lantern and for his general interest in the work. Finally, Mr. Humphry, of the Sir John Cass Institute, has devoted much time to obtaining the instantaneous photographs which accompany the communication. It is clear that by development of the photographic method much further information can be obtained, as the effects themselves are too transient for accurate examination.

CXIII. *On the Question of the Existence of Induction Effects from suddenly stopped Electrons, predicted by the Classical Theory.* By S. R. Milner, *F.R.S.*, *and* J. S. Hawnt, *M.Sc., Ph.D., University of Sheffield* *.

THE nature of the radiation process which occurs when a stream of moving electrons in an X-ray tube is suddenly stopped by the anticathode is a matter which is far from clear. On the classical theory of the production of X-rays, the radiation consists of a series of thin spherical pulses of electric and magnetic force spreading out radially from the stopped electrons. That such pulses can account for *all* the X-rays produced is an assumption that has now been abandoned, for there are features, *e.g.* the monochromatic character of part of the radiation, for which, clearly, it cannot account. The theory of *scattered* radiation, however, has long been based on the assumed existence of classical pulses, although recently even this limited application of the pulse theory has been rendered doubtful by Compton's work, which suggests that the scattered as well as the monochromatic radiation is unidirectional.

Fig. 1.



The investigation recorded here is an attempt to determine whether a certain effect which seems to be an essential consequence of the classical theory of radiation has or has not an existence in fact. The effect is as follows:—When an electron moving in the direction OA is suddenly stopped at a point A (fig. 1), on the classical theory a spherical electromagnetic pulse is propagated outwards from it. Inside the sphere the electric field is that of a stationary electron,

* Communicated by the Authors.

outside it that of the electron in motion, and, consequently, the field in the pulse itself (represented by lines joining those inside with those outside) has a component tending to move electrons in the direction OA. If this pulse were absorbed by the free electrons in a conducting cylinder XY, it should give them, on the average, a slight impetus in the direction OA, and a number of such pulses following one another sufficiently rapidly should result in the production in the cylinder of an e.m.f. tending to move electrons in the direction XY.

The theoretical magnitude of this e.m.f. in practical conditions is considerable. If e be the charge, v the velocity, and τ the duration of the stoppage of the electron, the tangential electric force in the pulse at the point B (r, θ) is, to a sufficient approximation,

$$\frac{ev}{c^2 r\tau}\sin\theta,$$

and the component of this parallel to OA is

$$\frac{ev}{c^2 r\tau}\sin^2\theta.$$

At any point where the pulse strikes the cylinder, this electric force lasts for a time τ and constitutes for a length dx of the cylinder an electromotive impulse of amount

$$\frac{ev}{c^2 r}\sin^2\theta\, dx = \frac{ev}{c^2 r}\sin^2\theta . \frac{r d\theta}{\sin\theta}.$$

Assuming, for simplicity, the cylinder to be of infinite length, and that half of it is screened by the anode, the total e.m.i. will be

$$\int_0^{\frac{\pi}{2}} \frac{ev}{c^2}\sin\theta\, d\theta = \frac{ev}{c^2}.$$

If n is the number of electrons stopped per second, the n e.m.i.'s are equivalent to a steady e.m.f.

$$\mathrm{E} = \frac{nev}{c^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let I be the current carried by the primary electrons, and V be the voltage drop in the tube, then $\mathrm{I} = ne$ and $\mathrm{V}e = \frac{1}{2}mv^2$, whence

$$\mathrm{E} = \frac{\mathrm{I}}{c^2}\sqrt{\frac{2\mathrm{V}e}{m}}.$$

This is in electrostatic units. If the e.m.f.'s are expressed in volts (V_v) and the current in amperes (I_a) we find, substituting

$$\frac{e}{m} = 5{\cdot}31 \times 10^{17} \text{ e.s.u.}, \quad I = \frac{c}{10} I_a, \quad V = \frac{1}{300} V_v,$$

$$E = 5{\cdot}95 \times 10^{-2} I_a \sqrt{V_v} \text{ volt.} \quad . \quad . \quad . \quad . \quad (2)$$

As a practical possible case, taking $V_v = 5000$ volts and $I_a = 10^{-3}$ ampere, we have

$$E = 4{\cdot}2 \times 10^{-3} \text{ volt.}$$

This is quite large, and if the two ends of the cylinder are joined by wires to a galvanometer, this portion of the circuit being screened from the pulses, it would be expected to produce a measurable current round the circuit.

When in an X-ray tube the stream of electrons moving with high velocities is stopped by the anode, the current is carried away in the metal by a large number of electrons moving with small velocities, and macroscopically the current in the tube is constant. Hence, we see that on the classical theory the existence of an e.m.f. of induction can be deduced, not only when the primary current is varying, but also in cases where it is *constant,* if the velocity of the electrons which carry it undergoes a sudden change.

This deduction from the classical theory has not, apparently, been noticed previously, and the existence or otherwise of the effect, so far as we know, has never been tested experimentally. Some years ago one of us made experiments to this end; they were negative, but, not being sufficiently conclusive, were not published. It may be stated here that the present more complete experiments have shown no evidence of the existence of the predicted e.m.f. under conditions where it might be expected to be easily observable.

Further consideration of the theoretical magnitude of the e.m.f.

The direct calculation of the e.m.f. on the principle employed above is somewhat illusory, and the numerical value to be expected in any experiment must be considerably reduced. The e.m.f. is independent of the thickness of the pulse but the energy radiated is not, being for each electron stopped

$$w = \frac{2}{3} \frac{e^2 v^2}{c^3 \tau},$$

or, if $s=\frac{1}{2}v\tau$ is the average distance over which the retardation takes place,

$$w=\frac{1}{3}\frac{e^2v^3}{c^3s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This gives for the total energy radiated, using the same substitutions as in equation (2),

$$W=\frac{1}{3}\frac{ne^2v^3}{c^3s}$$

$$=3{\cdot}7\times10^{-9}\frac{I_aV_v^2}{s}\text{erg/sec.} \quad . \quad . \quad . \quad . \quad (4)$$

By equating (4) to the greatest possible rate at which the e.m.f. can generate heat in the cylinder, an upper limit to the value of the e.m f. can be obtained. If k is the conductivity, t the thickness, r the radius, and l the length of the cylinder, the heat generated is $10^7 . E_v^2k . 2\pi rt/\text{erg/sec.}$ Thus from energy considerations,

$$E_v=<\left(\frac{Wl}{2 . 10^7 . \pi rtk}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Equations (4) and (5) show that the effective e.m.f. to be expected will be determined by the distance s in which the electrons are stopped *. The value of this is unknown, except that it may be expected to be of atomic or subatomic dimensions. Instead of attempting to estimate it we have used in equation (5) experimental data for the energy W. Beatty † has found experimentally that the energy W_x of the X-rays from a target is given by

$$W_x=2{\cdot}54\times10^{-4}A\left(\frac{v^2}{c^2}\right)W_e,$$

where A is the atomic weight of the target, v the velocity, and W_e the energy, of the exciting cathode rays. For a platinum anticathode (A=195) in a tube worked at 5000 volts and 10^{-3} ampere, $W_x=4{\cdot}9\times10^4$ erg/sec.

* According to equation (1) the e.m.f. is independent of the distance through which the electrons are accelerated or decelerated. It might be inferred, therefore, that *no* effect should be predicted by the theory, since the electrons are first accelerated to a velocity v and then retarded by their impact on the anode. It is clear, however, from the energy equation (4) that the acceleration effect will be quite negligible compared with that produced by the retardation.

† Proc. Roy. Soc. A, lxxxix. p. 314 (1914).

The classical pulses considered above were supposed to be produced by the stoppage of electrons which are all moving in the same direction. In reality an electron stopped by a target probably undergoes several collisions each with the emission of radiation; if so, it is only the first impact which would give rise to a pulse contributing to the e.m.f. In subsequent impacts the direction of motion of the electron would be changed, and the electromotive impulses due to these would not have any definite one way effect. In practice the X radiations emitted are incompletely polarized, and if this is due to the fact that a number of impacts contribute to the stopping of the electrons, some allowance ought to be made for this. Kirkpatrick* has investigated the dependence of the polarization on the voltage in an X-ray tube, and using his results we can infer that the polarization in the case we are considering (V = 5000 volts, Pt target) is approximately 30 per cent. Further, half the radiated energy will presumably be absorbed by the anode, and also in thin cylinders only a fraction of the energy will be absorbed. Allowing approximately for all these factors by taking in equation (5) as

$$W = \tfrac{1}{6} W_x (1 - e^{-\mu t}),$$

where μ is the absorption coefficient of the material of the cylinder, we obtained the following estimates of the maximum e.m.f.'s to be expected for the various anodes and cylinders employed, calculated for a tube voltage of 5000 volts and a current of 10^{-3} ampere.

Anode.	Cylinder.	Thickness (cm).	$1-e^{-\mu t}$.	Maximum e.m.f. (volts).
Pt	Pt	10^{-3}	·95	$2{\cdot}1\times10^{-3}$
Ni	Ni	10^{-2}	1	$2{\cdot}9\times10^{-4}$
Al	Ag	$2{\cdot}5\times10^{-7}$	·0003	$3{\cdot}6\times10^{-4}$

Experimental Arrangements.

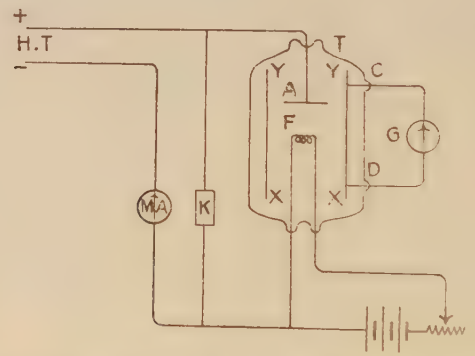
A glass tube T (fig. 2), connected to a mercury pump with carbon and liquid air for high exhaustion, contained a tungsten spiral F as cathode, a platinum anode A, and a thin platinum cylinder XY surrounding both. Long platinum leads were

* Phys. Rev. xxii. p. 229 (1923).

taken from the two ends of the cylinder to an oil-bath, where their junctions with the copper wires, leading to a very sensitive galvanometer G, were maintained at a constant temperature. The galvanometer circuit was carefully insulated from earth.

In the first experiments the electron current in the vacuum tube was produced by a motor generator, the voltage being measured with a Kelvin electrostatic voltmeter K and the current through the tube with a milliammeter MA. The motor generator was only capable of giving voltages up to 1100 volts. In order to extend the range of investigation to higher voltages in later experiments, an induction coil used with a valve to rectify the current was employed. By using condensers of different capacities in parallel with

Fig. 2.



the experimental tube, the voltage across it could be kept steady at prearranged values. It was measured by a specially constructed electrostatic voltmeter previously calibrated in terms of a spark-gap.

The earlier experiments showed that no dependable results could be obtained except from tubes at the highest exhaustions and with a pure electron discharge. Immediately a glow discharge started in the tube, considerable deflexions of the galvanometer ensued. These were readily traced in part to a thermo-electric effect in the platinum cylinder which becomes appreciably heated when a glow discharge occurs. With a pure electron discharge there is no heating of the cylinder except that due to radiation from the hot filament. The reason for the difference in heating of the cylinder in the two types of discharge is that, the cylinder and galvanometer being highly insulated, in the pure electron discharge the

cylinder rapidly becomes charged to such a potential that no further electrons can strike it. If, however, positive as well as negative ions exist in the tube, *i. e.*, if the discharge is of the glow type, ions of both signs can and do diffuse on to the metal of the cylinder, heating it up in a very marked way. Our observations have suggested that this diffusion of both ions together is the cause of much of the absorption of the gas in the glass and metal in vacuum tube discharge.

Experiments with pure electron discharges showed deflexions of the galvanometer when the current was started, but these could in each case be traced to causes other than the radiation pulses. A large part of the investigation consisted in the elimination of these effects, of which an account is now given.

(1) Although no thermo-electric effect should theoretically be present when the cylinder is formed of pure metal, nevertheless it was always observed. In the platinum cylinder it was in the same direction as the e.m.f. due to the pulses. It is easily distinguishable from the latter, because (*a*) it is established previous to the application of the voltage to the tube, (*b*) it forms and dies away slowly as the filament current is put on and off.

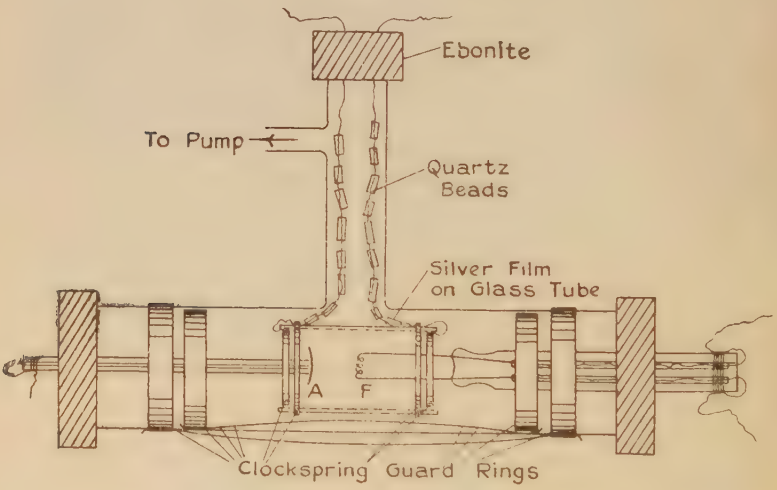
(2) When the electron current is passed through the tube the thermo-electric e.m.f. (1) may alter, due to the heating of the anode and the alteration of the temperature gradients in the cylinder. This effect again is easily distinguished by the slowness of its development, and it occurred to a measurable extent only when the current was of the order of several milliamperes.

(3) It is possible that there might be a current of ions in the tube from the cathode to the end X of the cylinder (fig. 2) and from Y to the anode. If it occurred this would give a deflexion of the galvanometer in the opposite direction to the theoretical e.m.f. At high pressures such an effect was always found, but on the establishment of sufficiently high vacua it was completely eliminated. It is clear that if only electrons are present in the tube, and if the cylinder cannot emit electrons, no permanent current can pass along it due to this cause. The cylinder and galvanometer, in fact, simply charge up statically to such a potential as will stop further electrons from being received. It was striking how immediately the apparent absence of positive ions in the tube could be recognized in exhaustion by the stopping of the current through the galvanometer due to this cause. It is true that at high voltages the cylinder will emit photo-electrons, and since these would come off chiefly from the end Y of the

cylinder this would allow a minute current to pass along it. This effect, however, was too small to be measurable.

(4) A more serious difficulty was caused by leakage along the walls of the tube. On switching on the voltage an electron current flows along the walls in the direction XY. This passes *via* the sealed-in joints through the cylinder and galvanometer in parallel. The current through the galvanometer is in the opposite direction to that due to the expected e.m.f. This formed a very serious difficulty which made its appearance with the earlier tubes at about 5000 volts, and with higher voltages this leakage current tended to mask entirely the effect under investigation. Guard-rings of tin-

Fig. 3.



foil placed round the outside of the tube at C and D (fig. 2) and connected metallically together eliminated the leakage to some extent, and enabled readings to be taken up to 10,000 volts without serious error. In later tubes the best arrangement was found to be attained by having a guard-ring inside and out (fig. 3). This enabled readings to be taken up to 20,000 volts without serious trouble from leakage of this type.

(5) An electrostatic induction effect will occur on establishing or removing the p.d. between the anode and the cathode. In the first event the sudden alteration of potential along the cylinder will result in an instantaneous flow of

electrons to neutralize it and keep the potential constant. The flow of these induced charges gives rise to a transient current through the galvanometer. At the higher voltages this effect became appreciable ; it is in the opposite direction to the deflexion resulting from the pulse e.m.f., but it could easily be distinguished from the latter by reason of its giving rise only to a throw of the galvanometer instead of to a steady deflexion.

Transient currents may also be induced in the galvanometer circuit by magnetic induction due to the establishment of both the primary and the secondary current of the induction coil. These also were very small, and being throws could not be mistaken for the effect under investigation.

Results.

The chief experiments have been made with three tubes containing respectively, a platinum anode and platinum cylinder, a nickel anode and nickel cylinder, an aluminium anode and silver cylinder. The first tube was designed all in platinum and glass so that it could be thoroughly cleaned, exhausted, and sealed off from the pump (fig. 2). The thermo-electric force effect (1) in this tube appeared very marked and cut down the possibility of using large electron currents, while leakage over the glass limited the voltage. The result of experiments showed that any e.m.f. produced in the cylinder was less than $1{\cdot}5 \times 10^{-5}$ volt at a tube voltage of 4·5 kv. and current 1·4 ma. The calculated value of the e.m.f. to be expected in these conditions is, in accordance with the calculations on p. 1189, about 3×10^{-3} volt. The actual magnitude of the calculated value is, of course, somewhat uncertain, but it is unlikely that it could be reduced to anything like the maximum value found possible experimentally.

In high atomic weight metals like platinum, the polarization of the X-rays emitted is not so great as in lower atomic weight elements, consequently experiments were carried out with nickel and aluminium anodes. In these tubes the leakage was much cut down by guard-rings, as described above. Further, it was realized that if the cylinder was so thick that the pulses were completely absorbed near the internal surface, the e.m.f. would be partly short-circuited by the outer layers of the cylinder. This pointed to the necessity, in order to make the investigation complete, of trying cylinders of different thicknesses. Experiments were

therefore made, using for the cylinder a thin silver film deposited on glass, in which there could be no possibility of such short-circuiting. In a series of readings with these tubes, in which the currents were varied up to 0·5 milliampere and the tube voltages up to 15 kilovolts, we found that the deflexions of the galvanometer were always very small (the *maximum* deflexion obtained was 0·7 cm. corresponding to $1{\cdot}1 \times 10^{-5}$ volt), and, moreover, were always in the direction *opposite* to that which would be given by the theoretical e.m.f.*. The experiments thus showed no trace of the effects of the theoretical e.m.f., although its magnitude may be estimated in these conditions to extend up to 10^{-3} volt at the highest current and voltage.

These experiments demonstrate the absence of the e.m.f. predicted by the classical theory, and afford a conclusive proof that the picture of the process of radiation, or at any rate of absorption, on which its derivation was based is erroneous. They add now, it is true, but another piece to a considerable body of evidence that has come to light in this direction during the last few years. This evidence appears to show that radiation occurs in directed quanta and not in spreading pulses. The result of the present experiments, while by no means proving it, is consistent with the quantum view; for if the absorption occurs sporadically at individual electrons (including those in the atoms) it would not be expected to give rise to the e.m.f. which would result if the pulse acted, as on the classical theory it should, on the free electrons present in the metal. The view of absorption by quanta is undoubtedly necessary as regards the homogeneous X radiation, where the electrons which are set in motion appear to be solely those which are ejected from atoms which absorb whole quanta. As regards the non-homogeneous radiation, however, certain experiments, particularly Barkla's on the intensity of scattered radiation in various directions, have until recently appeared to be most easily accounted for by the classical theory of spherical pulses. The present experiments, even at the present time, have therefore some value in showing that an effect predicted by this theory is absent in actual practice.

We wish to thank the Department of Scientific and Industrial Research for aid given to one of us towards this research.

* These small remaining deflexions were probably due to the leakage over the glass not being completely eliminated.

Summary.

If the radiation from the moving electrons in a vacuum tube when they are suddenly stopped by the anode consists of the spherical pulses of the classical theory, an e.m.f. should be generated in a metal cylinder surrounding the anode ; considerations of the energy of the pulses set a limit to the magnitude of the e.m.f. which is, nevertheless, of such a value that it should be capable of being detected by a suitably-arranged galvanometer.

The experiments show no trace of the existence of such an e.m.f. and add further evidence to the view that pulses of the kind formulated by the classical theory, if they exist, are not absorbed in accordance with classical considerations.

CXIV. *On Poisson's and Lexis's Problem of Probability of Repeated Trials.* *By* Charles Jordan, *D.Sc.**

I. Poisson's Problem.

1. LET p_1 be the probability that an event will happen at the first trial, p_2 that it will happen at the second, and so on, p_n that it will happen at the nth trial ; let $q_1, q_2, \ldots q_n$ be the corresponding probabilities for failures.

Let us denote by P_x the probability that the event will happen x times in n trials. It is known that this probability is equal to the coefficient of t^x in the expansion of the product

$$\phi(t) = \prod_{i=1}^{n} (q_i + p_i t) = \sum_{x=0}^{n} P_x . t^x; \quad . \quad . \quad . \quad (1)$$

i. e., $\phi(t)$ is the *generating function* of the probability P_x.

2. Let $\psi(m, x)$ denote the quantity $e^{-m}m^x/x!$, and G_k the following polynomial in x of the kth degree †

$$G_k = \frac{1}{\psi(m, x)} \frac{d^k}{dm^k} \psi(m, x).$$

* Communicated by the Author.

† Ch. Jordan, "Développements nouveaux pour l'application du théorème de Bernoulli," *Comptes Rendus*, Paris, 1926, p. 303; and "Sur la probabilité des épreuves répétées, le théorème de Bernoulli et son inversion," *Bulletin de la Société Mathématique de France*, 1926.

Hence

$$G_0 = 1, \quad G_1 = \frac{1}{m}\left[\binom{x}{1} - m\right],$$

$$G_2 = \frac{2!}{m^2}\left[\binom{x}{2} - \frac{m}{1}\binom{x}{1} + \frac{m^2}{2!}\right],$$

$$G_k = \frac{k!}{m^k}\sum_{\iota=0}^{k}(-1)^{\iota}\binom{x}{k-\iota}\frac{m^{\iota}}{\iota!}. \quad . \quad . \quad . \quad . \quad (2)$$

It can be shown that

$$\sum_{x=0}^{\infty} G_k G_s \psi(m, x) = 0 \quad \text{if } k \neq s \text{ and } \sum_{x=0}^{\infty} G_k^2 \psi(m, x) = \frac{k!}{m^k}.$$

. . . (3)

Thus the G polynomials are orthogonal; therefore a function $y=f(x)$ in which x takes the values 0, 1, 2, 3, ... ∞ can easily be expanded as the following series:

$$y = [a_0 + a_1 G_1 + a_2 G_2 + \ldots]\,\psi(m, x), \quad . \quad . \quad (4)$$

where the coefficients a_s are functions of the disposable parameter m, and independent of x. From relation (3) it follows that

$$a_s = \frac{m^s}{s!}\sum_{x=0}^{\infty} G_s . y.$$

If $\mathfrak{M}_s$ denotes the factorial moment of y of the sth order

$$\mathfrak{M}_s = \sum_{x=0}^{\infty} x(x-1)(x-2)\ldots(x-s+1) . y,$$

then, according to (2), a_s is given by the following symbolical expression:

$$a_s = \frac{1}{s!}(\mathfrak{M} - m)^s, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where, after expansion, $\mathfrak{M}_\iota$ must be put instead of $\mathfrak{M}^\iota$.

3. The probability P_x can rigorously be expanded as the series (4), if we put $y = P_x$ for $x = 0, 1, 2, \ldots n$, and $y = 0$ for $x > n$. Moreover, let m be the mean value of x; *i. e.*,

$$m = \sum_{x=0}^{n} x . P_x = \mathfrak{M}_1.$$

It is easy to see that the factorial moment of P_x of the sth order is

$$\mathfrak{M}_s = \left[\frac{d^s}{dt^s}\phi(t)\right]_{t=1}; \quad \ldots \quad (6)$$

i. e., $\mathfrak{M}_s$ is the sth derivative of the generating function (1), with respect to t, in which t has been put equal to 1. Hence

$$\mathfrak{M}_0 = 1, \quad \mathfrak{M}_1 = \Sigma p_i = m, \quad \mathfrak{M}_2 = (\Sigma p_i)^2 - \Sigma p_i^2,$$
$$\mathfrak{M}_3 = m^3 - 3m\Sigma p_i^2 + 2\Sigma p_i^3,$$
$$\mathfrak{M}_4 = m^4 - 6m^2\Sigma p_i^2 + 8m\Sigma p_i^3 - 6\Sigma p_i^4 + 3(\Sigma p_i^2)^2, \ldots.$$

According to (5), the coefficients a_s of the expansion of P_x will be

$$a_0 = 1, \quad a_1 = 0, \quad a_2 = -\tfrac{1}{2}\Sigma p_i^2, \quad a_3 = \tfrac{1}{3}\Sigma p_i^3,$$
$$a_4 = \tfrac{1}{8}[(\Sigma p_i^2) - 2\Sigma p_i^4], \ldots.$$

The general form of a_s is given by the symbolical expression (5).

Finally, the required expansion will be

$$P_x = [1 - \tfrac{1}{2}\Sigma p_i^2 \,.\, G_2 + \tfrac{1}{3}\Sigma p_i^3 \,.\, G_3$$
$$- \tfrac{1}{8}[(\Sigma p_i^2)^2 - 2\Sigma p_i^4]G_4 + \ldots]\psi(m, x). \quad (8)$$

If a sufficient number of terms is calculated, any required degree of precision may be attained. Generally a few terms will give P_x correct to the third or fourth decimal.

4. The probability that the number of successes in n trials does not exceed the number χ can be deduced from formula (8) by applying the theorem of total probabilities

$$P(\chi) = \sum_{x=0}^{\chi} P_x.$$

It can be shown that

$$\sum_{x=0}^{\chi} G_s(m, x) \,.\, \psi(m, x) = -G_{s-1}(m, \chi) \,.\, \psi(m, \chi);$$

moreover, that

$$\sum_{x=0}^{\chi} \psi(m, x) = 1 - I(u, \chi),$$

where $u = m / \sqrt{\chi + 1}$ and $I(u, \chi)$ is the ratio of the incomplete Γ-function to the complete *.

* K. Pearson, 'Tables of the Incomplete Γ-Function,' London, 1922.

Finally the result will be :

$$P(\chi) = 1 - I(u, \chi) - [a_2 G_1 + a_3 G_2 + a_4 G_3 + \ldots]\psi(m, \chi).$$

This expression is also rigorous.

Remark.—The numerical valuation of $G_s\psi(m, x)$ is much simplified by the relation

$$G_s\psi(m, x) = (-1)^s \Delta^s \psi(m, x-s),$$

as there are tables which give the values of $\psi(m, z)$ *, and from them it is easy to compute the above differences.

II. Lexis's Problem.

4. Let us suppose that the probability of the single event is the same at each of n trials, and that it is equally likely that this probability is equal to p_1 or p_2 or $p_3 \ldots$ or p_ω ; let $q_1, q_2 \ldots q_\omega$ be the corresponding probabilities of failures.

If we denote by $P(x)$ the probability that the event will happen x times at n trials, we have

$$P(x) = \frac{1}{\omega} \sum_{i=1}^{\omega} \binom{n}{x} p_i^x q_i^{n-x}.$$

The generating function of this probability is

$$\phi(t) = \frac{1}{\omega} \sum_{i=1}^{\omega} (q_i + p_i t)^n. \quad . \quad . \quad . \quad . \quad (10)$$

The factorial momentum of $P(x)$ can easily be deduced from (10) by aid of formula (6)

$$\mathfrak{M}_s = \frac{1}{\omega} n(n-1)(n-2)\ldots(n-s+1) \sum_{i=1}^{\omega} p_i^s.$$

If we put $\frac{1}{\omega}\Sigma p_i = p$ and $np = m$, it results

$$\mathfrak{M}_0 = 1, \quad \mathfrak{M}_1 = m, \quad \mathfrak{M}_2 = \frac{1}{\omega} n(n-1)\Sigma p_i^2,$$

$$\mathfrak{M}_3 = \frac{1}{\omega} n(n-1)(n-2)\Sigma p_i^3, \text{ etc.}$$

The probability $P(x)$ can now be expanded in a series (4),

* K. Pearson, 'Tables for Statisticians and Biometricians,' pp. 113-121. Cambridge, 1914.

where the coefficients a_i are given by formula (5):

$$a_0 = 1, \quad a_1 = 0, \quad a_2 = \frac{1}{2}\left[\frac{1}{\omega} n(n-1)\Sigma p_i^2 - m^2\right],$$

$$a_3 = \frac{1}{6}\left[\frac{1}{\omega} n(n-1)(n-2)\Sigma p_i^3 - \frac{3}{\omega} mn(n-1)\Sigma p_i^2 + 2m^3\right],$$

etc.

Formula (9) gives, by aid of the above coefficients, the expansion of the probability that the number of successes in n trials does not exceed χ.

Both expansions are rigorous, and if the necessary number of terms are calculated, any prescribed precision can be obtained.

CXV. *The Difference in the Time Lags in the Disappearance of the Electric Double Refraction behind that of the Electric Field in several Liquids.* *By* J. W. Beams, *Ph.D., National Research Fellow, University of Virginia, and* Fred Allison, *Ph.D., Professor of Physics, Alabama Polytechnic Institute*.*

When an electric field is applied across two metallic plates immersed in a liquid such as carbon bisulphide or chloroform, the liquid between the plates becomes doubly refracting. This phenomenon was discovered by Kerr † and is usually referred to as the "Kerr Effect." If the electric field is suddenly relaxed, the electric double refraction disappears very quickly. In the case of carbon bisulphide, Abraham and Lemoine ‡ have concluded that the electric double refraction follows without any lag the variations of the electric field which produces it. Their experiments, however, are subject to considerable uncertainty because of phenomena occurring at the beginning of the spark discharge which make their measurements unreliable §. Wood ‖, on the other hand, noted in his experiments that, when nitrobenzene was substituted for carbon bisulphide, the electric double refraction seemed to

* Communicated by the Authors.

† Kerr, Phil. Mag. vol. i. pp. 337, 446 (1875); vol. vii. pp. 85, 229 (1879).

‡ Abraham and Lemoine, *Comp. Rend.* t. cxxx. p. 499 (1900).

§ Brown and Beams, J. Opt. Soc. Amer. and Review of Scientific Instruments, vol. xi. p. 11 (1925); Beams, Phys. Rev. vol. xxviii. p. 475 (1926).

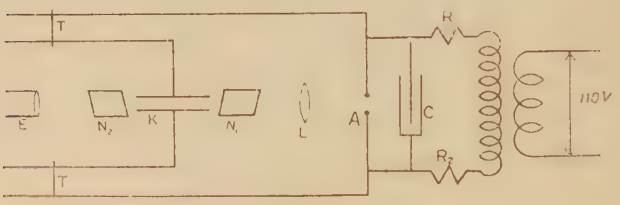
‖ Wood, Proc. Roy. Soc. A, vol. xcix. p. 371 (1921).

die away less rapidly. Recently *, preliminary mention of a method has been made by which the difference in the time lags of the electric double refraction behind the relaxation of the electric field could be detected; but the method did not lend itself to accurate quantitative measurements.

Since accurate quantitative data on these time lags are necessary for the application of the quick decay of electric double refraction to the measurement of short time intervals, as well as for the establishment of a satisfactory theory of the "Kerr Effect," the above-mentioned method has been improved and extended to the precise determination of the difference in the time lags in the disappearance of the electric double refraction behind that of the electric fields. This paper describes the method and gives the experimental results for carbon bisulphide, chloroform, and bromoform.

To understand the method of the experiment, consider fig. 1. K is a so-called "Kerr Cell" made by immersing

Fig. 1.



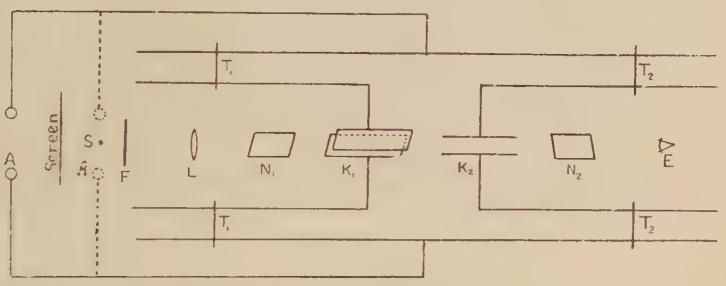
two parallel plates of metal in a liquid such as carbon bisulphide. N_1 and N_2 are crossed nicols, the diagonals making an angle of 45° with the plates of K. If an electric field is applied across the spark-gap A and consequently across the plates of K, light will pass N_2 so long as the field is applied, but no light will pass N_2 if the field is relaxed. It has been found † that if the electric field in K is relaxed by the spark at A, no light from A passes N_2 provided the lead wires are made very short. If, however, the lead wires from A to K are lengthened, light from A passes N_2, *i. e.*, the closing of K can be advanced or retarded with respect to a spark at A simply by shortening or lengthening the lead wires from A to K.

* Beams, J. Opt. Soc. Amer. and Review of Scientific Instruments, vol. xiii. p. 957 (1926).

† Brown and Beams, J. Opt. Soc. Amer. and R. S. I. vol. *xi.* p. 11 (1925); Beams, Phys. Rev. vol. xxviii. pl 475 (1926).

The arrangement of the apparatus used in this experiment is shown in fig. 2. K_1 and K_2 are "Kerr Cells" of practically identical dimensions, the plates being 12 cm. in length, 1 cm. in width, and 0·45 cm. apart. The plane of the plates of K_1 is vertical, while that of K_2 is horizontal. These cells are so constructed that the liquid with which they are filled can easily be removed and another substituted. N_1 and N_2 are crossed nicols as before, L is a lens which renders the light from a steady source S parallel, and F is a light filter which makes the light from S practically monochromatic. T_1 T_1 and T_2 T_2 are cross-wires by means of which the lead wires from the spark-gap A to K_1 and to K_2, respectively, can be lengthened or shortened by the observer at E. The lead wires from A to K_2 are so arranged that K_2 can be moved in the direction SN_1N_2 four or five metres without changing their length or their distances apart. The source of high

Fig. 2.



potential applied across the spark-gap A was either a 60-cycle, 10,000-volt transformer or an induction coil.

Suppose that K_1 and K_2 are first filled with carbon bisulphide and the high potential is slowly applied across A. The electric fields across K_1 and K_2 are therefore equal during the time of charging. Hence, since K_1 and K_2 are identical and the planes of their plates are at right angles, the electric double refraction in K_1 is exactly compensated by that in K_2 and no light from S passes N_2 during the charging. In the case of a sudden discharge of K_1 and K_2 through the spark-gap A, no light will pass N_2 if the lengths of the lead wires from A to K_1 are equal to, and symmetrical with, those from A to K_2, *i.e.*, the electric double refraction in K_1 at every instant is compensated by that in K_2. On the other hand, if K_2 by lengthening the lead wires from A to K_2 is made to discharge a certain time after K_1, light will pass N_2. If now K_2 is moved backward

in the direction AN_1N_2, (although not so shown in fig. 2, N_2 was about five metres behind N_1; the distance, of course, separating N_2 and N_1 is immaterial), it is possible to find a position of K_2 for which no light passes N_2. The distance through which K_2 must be moved backward to secure compensation was found to be equal to the total increase of lead wire from A to K_2, *i. e.*, the electric impulse travelled along the lead wires at approximately the velocity of light, a finding which is in agreement with many well-known results.

To increase the precision of these experiments a very strong source of light is required at S. It has been previously shown* that with the above arrangement of apparatus it is possible to pick out of the zinc spark the zinc-spark lines 4912·24 A. practically alone, and that they are very intense for a few hundred millionths of a second, depending upon the auxiliary capacity in parallel with the spark. The steady light-source S was therefore removed and the spark-gap A was clamped in its place, as shown by the dotted lines in fig. 2. Zinc electrodes were put in the terminals of the spark-gap A, and a variable capacity was connected in parallel to make the spark more intense. The lead wires AT_1K_1 and AT_2K_2 were then adjusted so that, when K_2 was placed directly behind K_1 and T_2T_2 were moved a few metres forward and backward from the position of complete extinction, the lines 4912·24 A. passed N_2. T_2T_2 were then moved to the position of complete extinction, *i. e.*, where the nicol N_2 transmitted no light. Chloroform was then substituted in K_2 for carbon bisulphide, and the plane of K_2 was rotated through an angle of 90°. (This adjustment is necessary, since chloroform behaves in an electric field as a negative uniaxial crystal and carbon bisulphide as a positive uniaxial crystal.) It was then found that light passed N_2, but that if K_2 was moved backward a distance of 100 cm., practically no light passed N_2, *i. e.*, the electric double refraction in carbon bisulphide is practically compensated by that in chloroform, resulting from the fact that the Kerr constant of carbon bisulphide is almost equal to that of chloroform. (It is not necessary that the Kerr constants of two liquids be equal in order to secure compensation when monochromatic light is used, since by rotating the planes of the plates of K_1 and of K_2 with respect to N_1 the magnitude of the double refraction in K_1 and K_2 can be varied.)

When the two cells contained carbon bisulphide and the

* Beams, *loc. cit.*

lead wires were so adjusted that N_2 extinguished the light, K_2 being immediately behind K_1, the electric fields in K_1 and K_2 were then relaxed together; or, to be exact, the electric field in K_1 was relaxed before that in K_2 by a time equal to the distance between the centres of the cells divided by the velocity of light. When chloroform was substituted for carbon bisulphide, the electric fields in K_1 and K_2 were still removed practically together as in the case of carbon bisulphide; but since it was found necessary to move K_2 back a distance of 100 cm. in order to extinguish the light through N_2, the disappearance of the electric double refraction in chloroform must lag behind that in carbon bisulphide a time equal to 100 cm. divided by the velocity of light, or $3{\cdot}3 \times 10^{-9}$ sec. Similar experiments on the determination of time-lag differences of the electric double refraction behind the relaxing electric field were made for Bromoform. Table I. gives the results, together with the Kerr constants, the dielectric constants, and the coefficients of viscosity.

TABLE I.

Liquid.	Dielectric Constant.	Kerr Constant.		Coefficient of Viscosity at 20° C.	Difference in time lag of Kerr effect behind electric field.	
Carbon bisulphide, CS_2.	2·6	4·28	„	0·00367		
					100 cm.	$3{\cdot}3 \times 10^{-9}$ sec.
Chloroform, $CHCl_3$...	5·2	−4·01	„	0·00564		
					0 cm.	0 „
Bromoform, $CHBr_3$..	4·4	−3·8	„	0·20		

It will be noted from the table that the time lag in the liquids investigated does not depend, directly at any rate, upon the Kerr constant, the dielectric constant of the liquid, or the coefficient of viscosity. A great number of liquids, however, must be tested before definite conclusions can be drawn.

The fact that it was almost possible to extinguish completely the light through N_2 indicates that the double refraction remains constant for a definite time after the electric field is removed, and then decays abruptly. These abrupt decays must be similar in the cases so far investigated; otherwise a rather bright minimum would have occurred instead of almost complete extinction. The lack of complete extinction, however, probably indicates a small difference in the decay curves, and we hope to investigate this point further. The occurrence of this faint minimum instead of complete extinction might be

the result of the changes in capacity introduced in K_2 when the liquids were changed. However, this effect is very small and probably cannot completely account for the observed lack of perfect compensation.

We wish to thank Professor L. G. Hoxton for his interest in the work and for placing apparatus at our disposal.

Summary.

1. A method has been developed by means of which the difference in time lags of the disappearance of the electric double refraction after the removal of the electric field in various liquids can be measured with a precision of $0{\cdot}4 \times 10^{-9}$ sec.

(2) Of the liquids investigated, carbon bisulphide had the smallest lag, and is therefore probably the best liquid to use in experiments in which the decay of electric double refraction is used to measure small time intervals.

Rouse Physical Laboratory,
University of Virginia,
August 31, 1926.

CXVI. *Some Theoretical Determinations of Crystal Parameters.* *By* J. E. Lennard-Jones, *D.Sc., Reader in Mathematical Physics, and* Beryl M. Dent, *B.Sc., Research Assistant, The University, Bristol* *.

§ 1. *Introduction.*

THE complete specification of a crystal structure requires, in all but the very simplest cases, a knowledge not only of the shape and size of the unit cell but also of one or more crystal parameters. In the case of carbonate crystals, for example, the appropriate parameter is the distance between a carbon ion and an oxygen ion in a CO_3 group. The experimental determination of these parameters involves the comparison of the intensities of X-ray reflexion from a number of different planes of the crystal, and is in some cases a matter of considerable difficulty and uncertainty, as may be inferred from the widely varying results of different investigators. It is therefore of some interest to make, wherever possible, a theoretical determination of these parameters.

This has recently been done by the present authors for the carbonate crystals†. The method involves the calculation of

* Communicated by the Authors.

† Lennard-Jones and Dent, Roy. Soc. Proc. A, vol. cxiii. p. 673 (1927).

the absolute values of the crystal energies, and this requires a knowledge of all the forces operating between the different ions in the crystal. These forces have been classified under four headings, viz.: *electrostatic*, *van der Waals's attractive*, *polarization*, and *intrinsic repulsive* forces. The van der Waals's cohesive forces have been shown elsewhere * to be small compared with the electrostatic (valency) forces, and so need not be considered in crystals composed only of ions. The polarization of ionic cores due to the effective electrostatic charges of neighbouring ions introduces another system of forces, which may be calculated on the supposition that an electrical dipole is created at the centre of each ion. Many attempts have been made to determine the strength of these doublets in the various ionic cores, and their relation to the electric field which produces them, but no consistent results have yet been attained. There is, however, sufficient evidence to show that the polarization forces are small compared with the electrostatic and intrinsic repulsive forces, and their inclusion would constitute an approximation of the second order. In any case, where crystals possess a high degree of symmetry, the ionic cores are polarized symmetrically and the induced doublets are self-compensating. This is the case in the crystals considered in this paper, and so we shall omit the effect of polarization forces.

The intrinsic repulsive forces have been investigated by one of the present authors in a series of papers †, the last of which gives a complete table of the repulsive forces between pure gas atoms and between monovalent and divalent ions with electronic structures of the pure gas type.

The object of this paper is to use these intrinsic repulsive forces to make a theoretical determination of the parameters of three types of crystals, viz. (1) the Rutile group, (2) the crystals of Potassium Chlorostannate and Potassium Chloroplatinate, and (3) the crystal of solid carbon dioxide—all crystals of one parameter.

In the case of the Rutile group an attempt had previously been made by Born and Bollnow ‡ to determine theoretically the crystal parameter. The method was an adaptation of one used previously by Bragg and Chapman § in a theoretical

* *Cf.* Roy. Soc. Proc. A, vol. cvi. pp. 715 & 716 (1924).

† Lennard-Jones, Roy. Soc. Proc. A, vol. cvi. pp. 441, 463, & 709 (1924); vol. cvii. pp. 157 & 636 (1925); vol. cix. pp. 476 & 584 (1925); vol. cxii. p. 230 (1926).

‡ Born & Bollnow, *Naturwissenschaften*, vol. xiii. p. 559 (1925); and Bollnow, *Zeit. f. Phys.* vol. xxxiii. p. 741 (1925).

§ Bragg & Chapman, Roy. Soc. Proc. A, vol. cvi. p. 370 (1924).

study of the carbonate crystals. Like this method, it was devised to eliminate as far as possible the effect of the repulsive forces of the ions, which were then unknown. It has recently been shown that the omission of these forces in the carbonate crystals is not legitimate, for their inclusion makes considerable difference to the results*. It is found in this paper that the repulsive forces are equally important in the case of the Rutile crystals. Whereas the theoretical work of Born and Bollnow leads to the same crystal parameter for all the members of the Rutile group, this paper shows how the parameters vary from crystal to crystal, and the variation is in excellent agreement with experimental results.

The second type of crystal considered is that of Potassium Chlorostannate. This crystal and that of Potassium Chloroplatinate both possess a structure like that of fluorspar, the F^- ions of the latter corresponding to the K^+ ions, and the Ca^{++} ions to the $(SnCl_6)^{--}$ or $(PtCl_6)^{--}$ groups. The latter are to be regarded as units, each of which consists of Cl^- ions at the vertices of a regular octahedron with the positive ion in the centre. The axes of the octahedron coincide with the cubic axes. The parameter in this case is the ratio of the distance between metal and Cl ions in these groups to the side of the unit cell. The experimental value obtained for this parameter is 0·17 for $PtCl_6K_2$ † and 0·245 $SnCl_6K_2$ ‡, a difference which is surprising in view of the similarity in structure of the two crystals. It is interesting to find that the theoretical results obtained in this paper do not exhibit this large difference—in fact, the calculated parameters for both crystals agree almost exactly with the observed value for $PtCl_6K_2$.

The structure of solid carbon dioxide has been investigated by de Smedt and Keesom § and by Mark and Pohland ‖; but, whereas they agree as regards the type of lattice and the size of the elementary cell, they differ considerably in their estimate of the distance between adjacent C and O atoms. In order to interpret the distribution of X-ray intensities, Mark and Pohland calculate the scattering on the basis of heteropolar and homopolar binding in the CO_2 molecule. They find that they can obtain better agreement with homopolar binding, and with this assumption they

* Lennard-Jones & Dent, *loc. cit.*

† Scherrer & Stoll, *Zeit. f. Anorg. Chem.* vol. cxxi. p. 319 (1922).

‡ Dickinson, J. A. C. S. vol. xliv. p. 276 (1922).

§ Proc. Acad. Sci. Amsterdam, vol. xxvii. p. 839 (1924); and *Zeit. f. Krist.* vol. lxii. p. 312 (1925).

‖ *Zeit. f. Krist.* vol. lxi. p. 293 (1925).

give the distance C to O as 1·59 Å. De Smedt and Keesom, however, with the same assumption, find the distance to be 1·05 Å. In view of this discrepancy, it seems desirable to try to make a theoretical determination of the distance in question.

This can only be done when the nature of binding in the CO_2 molecule is known, and as there seems some doubt as to whether the molecule is homopolar or heteropolar the evidence in favour of each must be discussed.

Schaefer and Phillips* and Dennison† have each analysed the infra-red spectrum of gaseous CO_2, and have been led to definite conclusions regarding the size and form of the CO_2 molecule. As this method is independent of any special assumption regarding the disposition of the electrons in the group, and refers only to the internal vibrations and rotations of the nuclei, special weight must be given to their conclusions. They must, in fact, be regarded as checks on the results derived by other methods, especially when these involve a definite assumption with regard to the nature of the binding in the molecule. One such other method is the theoretical interpretation of the molecular refractivity and the scattering ratio of CO_2, and this theoretical work can proceed either on the basis of homopolar binding or on the basis of heteropolar binding. The former of these assumptions has been made by Ramanathan ‡, and this has led him to a value of 1 66 A. for the distance between the C and O nuclei in the CO_2 molecule. This is definitely higher than that obtained by any other method, and is inconsistent with the results of Schaefer (1·02 Å.) and Dennison (1·01 Å.) already mentioned. Havelock §, on the other hand, has recently considered the theory of molecular refractivities and their relation to the refractivities of the constituent atoms and ions, and, assuming heteropolar binding in the CO_2 molecule, has been led to results in accord with those of Schaefer and Dennison. The evidence therefore points to heteropolar binding in the CO_2 molecule.

We have therefore made theoretical calculations of the energy of crystalline CO_2 on the assumption that it consists of an array of C^{++++} ions and O^{--} ions. We are led to a value for the distance between C and O ions in the neighbourhood of 0·90 Å. At the same time we have calculated

* Schaefer & Philips, *Zeits. f. Phys.* vol. xxxvi. p. 641 (1926).

† Dennison, Phil. Mag. i. p. 195 (1926).

‡ Ramanathan. Proc. Roy. Soc. A, vol. cvii. p. 684 (1925); also *ibid.* A, vol. cx. p. 123 (1926).

§ Havelock, Phil. Mag. vol. iii. no. 13, p. 158 (Jan. 1927).

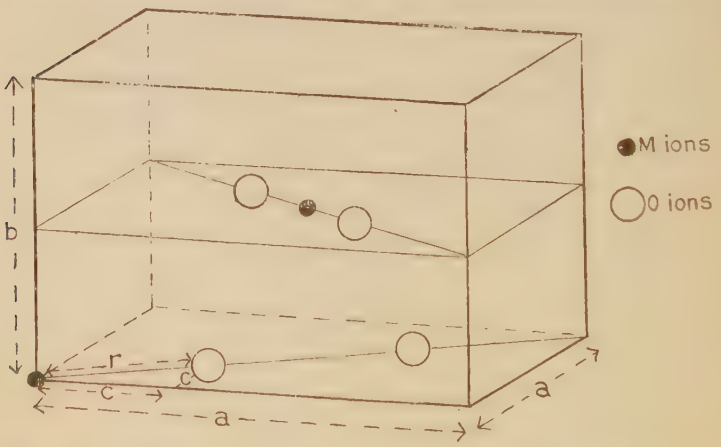
the heat of sublimation of CO_2 as a function of the parameter (distance C to O), and from a comparison of the observed value with this relation we are able to deduce a second value for the parameter which is in satisfactory agreement with the first. Both values are of the same magnitude as those of Schaefer and Dennison. The evidence of this paper, therefore, lends support to the crystal parameter determined by de Smedt and Keesom, as distinct from that obtained by Mark and Pohland.

§ 2. *Crystals of the Rutile Type.*

2.1. *Structure.*—Crystals of Rutile (TiO_2), Cassiterite (SnO_2), Polianite (MnO_2), and the dioxide of lead (PbO_2) all possess the same structure. The metal atoms form a space-centred tetragonal lattice, while the oxygen atoms lie in pairs, one on either side of a metal atom, such that the lines joining them are parallel to the diagonals of the base of the cell, as shown in fig. 1.

Fig. 1.

Unit cell of a crystal of the Rutile type containing two molecules.



The atoms are ionized, so that the metal atoms carry a fourfold positive charge and the oxygen atoms a double negative charge.

We use a to denote the side of the square base of the cell, b its height, and c the smallest coordinate distance between a metal ion and an oxygen ion and put

$$\beta = b/a, \quad \gamma = c/a.$$

We assume, as Bollnow does, that the lattice may be regarded as a "Koordinations-gitter"—that is, that the six oxygen atoms surrounding a metal atom are all at the same distance from it *. This gives a relation between the two parameters β and γ, so that the structure is completely defined by the length a and the parameter γ.

We denote the distance between a metal and an oxygen ion by r, so that $r = c\sqrt{2}$.

2.2. *Method.*—We now consider a displacement which keeps the distance r constant, calculate the potential energy of the crystal as a function of the parameter γ, and find the value of this parameter when the potential energy is a minimum. We then repeat this process for several different values of r, and thus obtain a curve connecting $\gamma_{\min.}$ with r.

2.3. *Calculation of the Potential Energy.*—In the introduction we pointed out that the only forces which need be taken into account are the electrostatic forces and the intrinsic repulsive forces; so that V, the potential energy of the crystal in ergs per molecule, may be written as the sum of two terms:

$$V = V^{(e)} + V^{(n)},$$

where $V^{(e)}$ is the contribution of the electrostatic forces and $V^{(n)}$ that of the repulsive forces. The term $V^{(e)}$ has been calculated by Bollnow for a series of values of γ. He writes the electrostatic potential energy of a cell containing two molecules (see fig. 1) as $= -\frac{2(2e)^2}{c} f_1(\gamma)$ †; so that in the notation of this paper

$$V^{(e)} = -\frac{(2e)^2}{c} f_1(\gamma).$$

We have therefore to deal with $V^{(n)}$ only. This contribution consists of three parts, $V_{MM}^{(n)}$, $V_{MO}^{(n)}$, and $V_{OO}^{(n)}$, which are the potential energies due to the repulsive forces between metal and metal, between metal and oxygen, and oxygen and oxygen respectively. The most important part of $V_{MO}^{(n)}$ is due to those atoms which are at a distance r apart, and since this distance is kept constant in the displacements we are considering we may assume that to a close degree of approximation $V_{MO}^{(n)}$ is constant. In order to calculate $V_{MM}^{(n)}$ we should have to know what are the repulsive forces

* For experimental evidence on this point, see Greenwood, Phil. Mag. xlviii. p. 654 (1924), and Vegard, Phil. Mag. i. p. 1151 (1926).

† Bollnow, *loc. cit.* pp. 747 & 755.

between the quadrivalent positive ions of each of the metals Ti, Mn, Sn, and Pb, and unfortunately we have at present no means of finding them. However, former work has shown that for a large number of cubic crystals * and also for carbonate crystals † the metal ions themseves make a negligible contribution to the potential energy of the crystal. In the case of $CaCO_3$, for example, the contribution is of the order of 0·1 per cent.‡. It is extremely likely that the same conclusion will also apply to the Rutile group of crystals. We therefore write

$$V^{(n)} = V_{OO}^{(n)} + \text{constant}.$$

2.4. *Calculation of* $V_{OO}^{(n)}$.—The repulsive action between two oxygen ions at a distance r apart may be represented by a force of the type $\lambda_{OO} r^{-n}$, where $\lambda_{OO} = 17{\cdot}6$ and $n = 11$ §. This value of λ_{OO} gives the force in dynes when the unit of length is the Ångström. The mutual potential energy of the two ions is therefore $\lambda_{OO}/10r^{10}$, and the potential of one O ion due to all the surrounding ions is $(\lambda_{OO}/10)\,\Sigma\, 1/r^{10}$. Since the force falls off so rapidly with the distance, it is sufficient to take into consideration only the nearest neighbours. We have considered the nearest forty. The distances are expressed as functions of γ and c, and then the quantity $\Sigma(1/r^{10})$ is calculated by direct summation for a series of values of the parameter γ. If we write $\Sigma(1/r^{10}) = f_2(\gamma)/c^{10}$, the values of $f_2(\gamma)$ are given in the following table :—

TABLE I.

Values of $f_2(\gamma)$ for the Rutile Group.

γ	0·27	0·28	0·29	0·300
$f_2(\gamma)$.....	$8{\cdot}47.10^{-3}$	$8{\cdot}58.10^{-3}$	$9{\cdot}03.10^{-3}$	$10{\cdot}08.10^{-3}$
γ	0·310	0·315	0·320	0·330
$f_2(\gamma)$.....	$12{\cdot}50.10^{-3}$	$14{\cdot}72.10^{-3}$	$18{\cdot}16.10^{-3}$	$31{\cdot}87.10^{-3}$

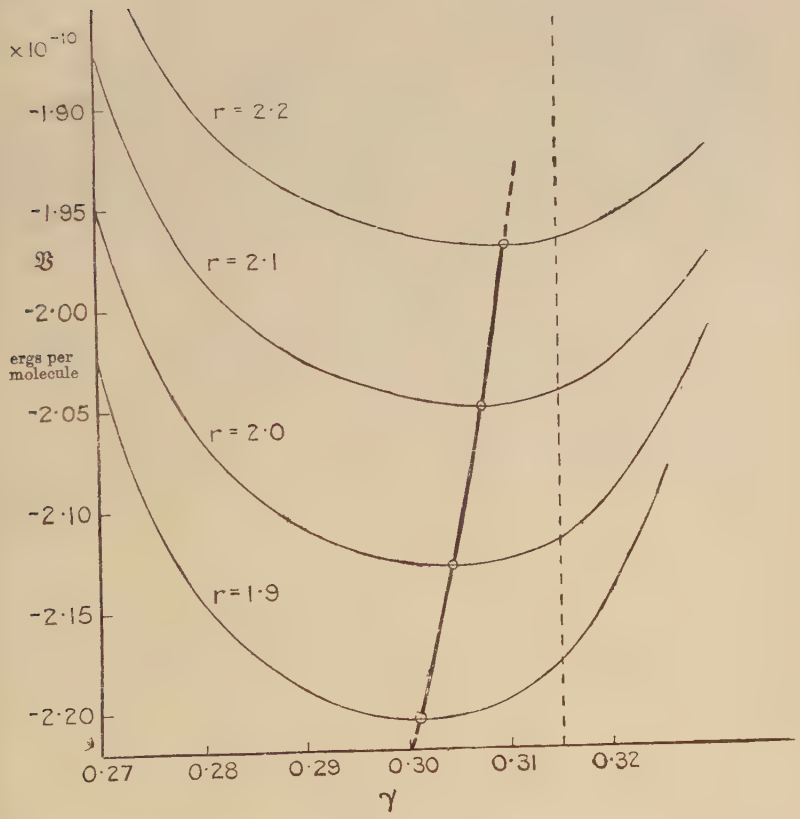
The potential energy of the crystal due to the repulsive forces between the oxygens is therefore

$$V_{OO}^{(n)} = (\lambda_{OO}/10c^{10}) f_2(\gamma) \text{ ergs per molecule.}$$

* Lennard-Jones & Taylor, Proc. Roy. Soc. A, vol. cix. p. 487 (1925).
† Lennard-Jones & Dent, *loc. cit.*
‡ *Loc. cit.* p. 689, Table viii. (U_{11}).
§ Lennard-Jones and Dent, Proc. Roy. Soc. A, vol. cxii. p. 230 (1926).

Fig. 2*.

The potential energy of crystals of the Rutile type for various configurations ($=\mathfrak{V}+$constant). The minimum of each curve gives a possible theoretical value of the crystal parameter. (The dotted line gives the corresponding result neglecting the intrinsic repulsive forces.)



* The value of $f_1(\gamma)$ for $\gamma=0{\cdot}29$ is of some importance in the determination of $\gamma_{\min.}$, as can be seen from fig. 2. Unfortunately, this value has not been calculated to the necessary degree of accuracy by Bollnow, as in his case the point is of less importance. The uncertainty thus caused in the curve in fig. 3 is about 0·001 for $r=1{\cdot}9$ and is less than this for greater values of r. This error is less than the variation in experimental accuracy.

2.5. *Determination of the Position of Stable Equilibrium.*—The total potential energy of the crystal, V, in ergs per molecule is therefore given by the following equations:

$$\begin{aligned} V &= V^{(e)} + V^{(n)} = V^{(e)} + V_{00}^{(n)} + \text{constant} \\ &= -\frac{(2e)^2}{c} f_1(\gamma) + (\lambda_{00}/10c^{10}) f_2(\gamma) + \text{constant} \\ &= \mathfrak{V} + \text{constant, say.} \end{aligned}$$

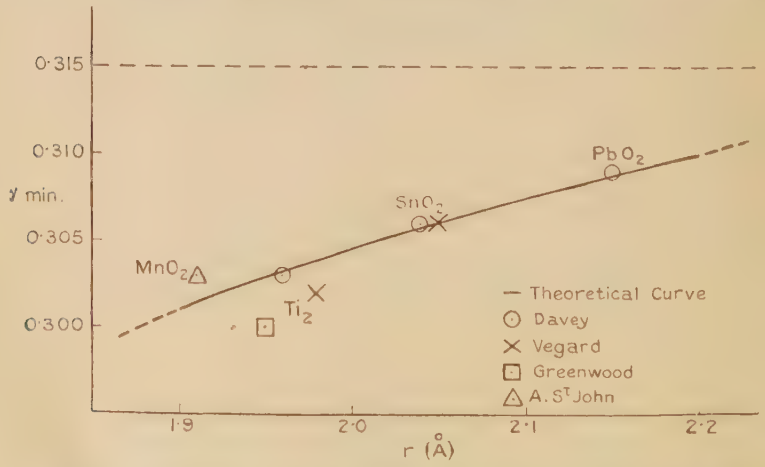
$\mathfrak{V}$ can now be expressed as a function of r by means of the equation $r = c\sqrt{2}$. If we assign a certain definite value to r, numerical values of $\mathfrak{V}$ can be found and plotted with γ as abscissæ. Four such curves are shown in fig. 2.

The value of γ corresponding to a minimum potential energy in each case can then be read off from the curves. We obtain in this way a relation between $\gamma_{\text{min.}}$ and r. This is shown in fig. 3 as a continuous line.

Fig. 3*.

The theoretical relation between the crystal parameter and the distance between metal and oxygen ions in the Rutile group. (The dotted curve is the theoretical relation obtained by Bollnow.)

The experimental results are taken or calculated from the work of Greenwood (Phil. Mag. vol. xlviii. p. 654, 1924), Vegard (Phil. Mag. vol. i. p. 1151, 1926), Davey (Phys. Rev. vol. xxiii. p. 763, 1924), and A. St. John (Phys. Rev. vol. xxi. p. 389, 1923).



2.6. *Discussion.*—The dotted line in fig. 3 gives the theoretical value obtained by Bollnow from a consideration of the electrostatic forces only. We see that by including the effect of the repulsive forces between the oxygen ions

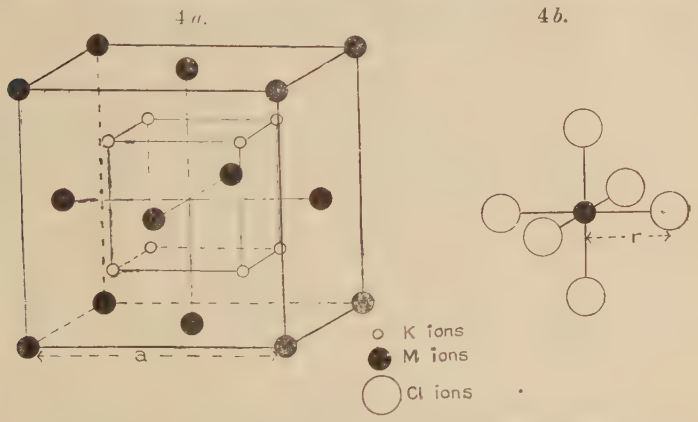
* For Ti_2 in the figure, read TiO_2.

the agreement with experiment is very much improved. The experimental points shown in fig. 3 are somewhat different from those given by Bollnow *, because some of the results included by him have recently been modified by more recent work †.

§ 3. *The Crystals of Potassium Chlorostannate and Potassium Chloroplatinate.*

3.1. *Structure.*—The structure of K_2SnCl_6 has been investigated by Dickinson ‡, and that of K_2PtCl_6 by Scherrer and Stoll §. In each case the structure resembles that of CaF_2 with K atoms in place of the F's, and the complex groups $SnCl_6$ or $PtCl_6$ in place of the Ca's. It will be convenient to refer to the Sn or Pt ions as M ions. We assume that the atoms are ionized, so that the K's have single positive charges, the Cl's single negative charges, and the M ions fourfold positive charges. In fig. 4*a* the positions of the M and K ions only are shown. Each M ion is surrounded by six Cl ions placed symmetrically on each of the 3 axes passing through it, as shown in fig. 4*b*.

Fig. 4.—Unit cell of K_2SnCl_6 (or K_2PtCl_6) containing four molecules.



The positions of the chlorines are determined by the parameter γ, such that the distance between an M ion and a Cl ion is equal to γ times the edge of the unit cube containing four molecules—that is, to γa. We denote this distance by r.

* Bollnow, *loc. cit.* fig. 5.
† Vegard, Phil. Mag. vol. i. p. 1151 (1926).
‡ *Loc. cit.* § *Loc. cit.*

3.2. *Method.*—We consider a displacement which keeps the distance r constant, and just as in the case of rutile, we calculate the potential energy of the crystal as a function of the parameter γ, and find the value of this parameter when the potential energy is a minimum. The process is repeated for several different values of r. We finally obtain a curve connecting $\gamma_{\min.}$ with a.

As before, we write the potential energy

$$V = V^{(e)} + V^{(n)};$$

but in this case we have to calculate $V^{(e)}$ as well as $V^{(n)}$. In calculating $V^{(n)}$ we take into account the repulsive forces between the Cl ions of one group and those of neighbouring groups, between Cl ions and K ions and between K ions themselves. As before, we omit the effect of the forces between metal ions alone *, and we also omit the effect of the metal ion of one group on the Cl ions of other groups. We can then write

$$V^{(n)} = V^{(n)}_{ClCl} + V^{(n)}_{ClK} + V^{(n)}_{KK} + \text{constant}.$$

The constant refers to the interaction between Cl and metal ions of the same group.

Hence, in order to find the potential energy, we have to calculate the four quantities $V^{(e)}$, $V^{(n)}_{ClCl}$, $V^{(n)}_{ClK}$, and $V^{(n)}_{KK}$.

3.3. *Calculation of the Electrostatic Potential Energy* ($V^{(e)}$).—We wish to calculate $V^{(e)}$ in ergs per molecule as a function of r, and we follow a method due to Emersleben †. He has given a table of values for Born's "Grundpotential" which makes it possible to calculate the potential energy of any crystal whose unit cell can be built up of smaller cells determined by the vectors a_1, a_2, a_3, such that the sides of the unit cell are $=na_1, na_2, na_3$, where $n=1, 2, 3, \ldots 12$, and so that there are no charges anywhere in the unit cell except at the corners of some or all of the smaller cells. It can be seen by examining fig. 4 that it is possible to calculate by this method the potential energy for the values $\gamma=3/12$ and for the two neighbouring values $\gamma=2/12$ and $4/12$. In the first case it is sufficient to take $n=4$, but for the last two we must take $n=12$.

Now the electrostatic potential energy of all lattice points on one cell is equal to twice the electrostatic energy of the

* *Cf.* footnotes on p. 1210.

† Emersleben, *Phys. Zeit.* xxiv. pp. 73 & 97 (1923).

lattice per cell. In Born's notation *,

$$\phi_0 = \mathop{\mathrm{S}}_{l} \Sigma'_{kk'} \frac{e_k e_{k'}}{\mathrm{R}^{l}_{kk'}}.$$

Emersleben writes

$$\psi = \tfrac{1}{2}\phi_0 = \frac{e^2}{2a} \Sigma \pi\left(\frac{p}{n}\right) \mu_p,$$

where a is the smallest coordinate distance between ions, and $\pi\left(\frac{p}{n}\right)$ is Born's "Grundpotential." The summation is extended over a cube of side na; p is a vector giving the position of a lattice point whose coordinates are $(p_1 a, p_2 a, p_3 a)$, and μ_p is connected with the distribution of charges in the cell by means of the equations :

$$\begin{aligned} e^2 \mu_p &= \Sigma\, \xi_p, \\ \tfrac{1}{2} \mathrm{N} \xi_p &= \mathrm{A}^2 + \mathrm{B}^2, \qquad (\mathrm{N} = n^3), \\ \left\{ \begin{aligned} \mathrm{A}\left(\frac{p}{n}\right) &= \Sigma_q \frac{\epsilon_q}{e} \cos 2\pi \left(\frac{qp}{n}\right), \\ \mathrm{B}\left(\frac{p}{n}\right) &= \Sigma_q \frac{\epsilon_q}{e} \sin 2\pi \left(\frac{qp}{n}\right), \end{aligned} \right. & \quad (qp) = (q_1 p_1 + q_2 p_2 + q_3 p_3), \end{aligned}$$

where ϵ_q is the charge at the lattice point q and all the summations extend over the unit cell.

The values of $\pi\left(\frac{p}{n}\right)$ have been tabulated †, and we have therefore only to calculate the values of μ_p. In order to do this we must write down the coordinates (p_1, p_2, p_3) of all the lattice points in the unit cell—n^3 in number—the coordinates q_1, q_2, q_3 of all the charges, and evaluate the summations for A and B. It seems at first sight as if the work would be very long, since there are 1728 lattice points in the two cases when $n=12$; but it can be very much simplified—firstly, by considering the symmetrical properties of the π's and of the crystals considered, and, secondly, by formulating, for $\gamma=2/12$ and $4/12$, rules by which the values of A and B can be written down for the various types of p's which occur ‡. The results of the calculation are given in the

* Born, 'Atomtheorie des festen zustandes,' p. 714, equation (397).

† Emersleben, *loc. cit.*, and Born, *loc. cit.* p. 782.

‡ For example, when $\gamma=2/12$, B=0 for all p's, and A=0, unless the p's are all even or all odd. If, when the p's are all odd, we put $a=1$ or 7, $b=3$ or 9, $c=5$ or 11, then we have the following types of combination: *aaa, aab, aac, abb, abc, acc, bbb, bbc, bcc, ccc.* The corresponding values of A are found to be 4, 16, 4, 28, 16, 4, 40, 28, 16, 4 respectively.

following table, where $r=\gamma a$. In our notation $\psi=V^{(e)}$ ergs per molecule. We write

$$V^{(e)}=\frac{f_1(\gamma)}{r}.10^{-18}.$$

TABLE II.

Values of $f_1(\gamma)$ for K_2SnCl_6 or K_2PtCl_6.

γ	2/12	3/12	4/12
$f_1(\gamma)$	−3·606	−3·617	−2·812

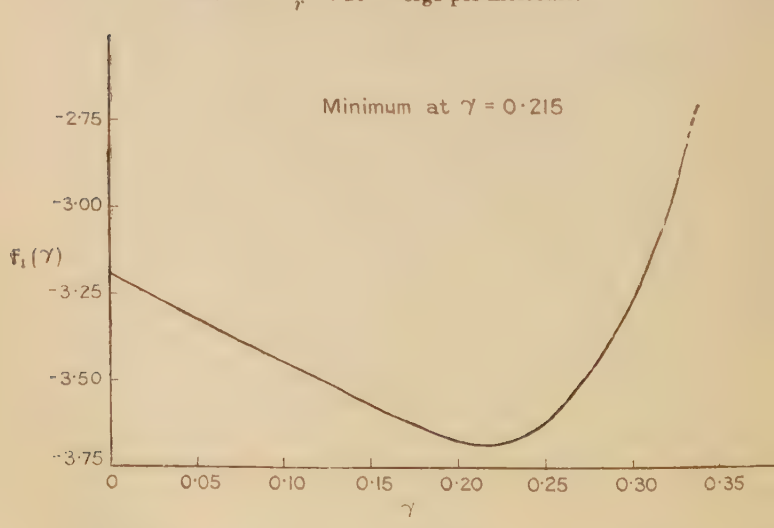
As γ tends to 0, with r fixed, a tends to infinity, and therefore the potential energy tends to the potential energy of one MCl_6 group. This is equal to

$$\frac{6(-4e^2)}{r}+3\left(\frac{e^2}{2r}+\frac{4e^2}{\sqrt{2}r}\right) \qquad \text{(see fig. 4 } b\text{)}$$
$$=-\frac{3\cdot194}{r}.10^{-18}.$$

Fig. 5.—Curve of $f_1(\gamma)$.

The electrostatic potential energy of $SnCl_6K_2$, or $PtCl_6K_2$,

$$=V^{(e)}=\frac{f_1(\gamma)}{r}.10^{-18} \text{ ergs per molecule.}$$



The function $f_1(\gamma)$ is plotted in fig. 5. Values of $f_1(\gamma)$ for $\gamma=0\cdot20$, $0\cdot225$, and $0\cdot30$ have been obtained by the use of an interpolation formula.

3.4. *Calculation of* $V^{(n)}$.

(i.) $V^{(n)}_{ClCl}$. Assuming the repulsive force between two Cl ions to be $\lambda_{ClCl}r^{-n}$, λ_{ClCl} has been found to be 4·49 and $n=9$ *. This gives the force in dynes when the distance is measured in ångströms. The potential energy of the six Cl's of one MCl_6 group due to the repulsive forces of all the surrounding Cl's is therefore equal to $(\lambda_{ClCl}/8)(\Sigma r^{-8})$, and the potential energy of the crystal due to the repulsive forces between the Cl ions, in ergs per molecule $= V^{(n)}_{ClCl} = (\frac{1}{2}\lambda_{ClCl}/8)(\Sigma 1/r^8) + \text{constant} = \mathfrak{V}^{(n)}_{ClCl} + \text{constant}$, say, where the constant represents the interaction of the Cl's of the same group. We have considered the effect of the Cl's of the eighteen nearest groups. This involves 648 distances, 15 of which are different. These are expressed as functions of γ and r, and $V^{(n)}_{ClCl}$ is calculated by direct summation for a series of values of the parameter γ.

(ii.) $V^{(n)}_{ClK}$. In a similar way we find the potential energy of the six Cl's of one group due to the repulsive forces of all the surrounding K's to be $(\lambda_{ClK}/8)(\Sigma 1/r^8)$, and $V^{(n)}_{ClK} = 2 \cdot \frac{1}{2}(\lambda_{ClK}/8)(\Sigma 1/r^8)$, the factor 2 being necessary because there are two K ions in a molecule. We have considered the 32 nearest K's, that is 192 distances, 6 of which are different.

(iii.) $V^{(n)}_{KK}$. The K ions alone form a simple cubic structure, and so the potential energy of one K due to all the rest can be expressed in the form

$$\lambda_{KK}A^{(n-1)}/(n-1)\left(\frac{a}{2}\right)^{(n-1)},$$

where A is a crystal potential constant †. Therefore

$$V^{(n)}_{KK} = \tfrac{1}{2} \cdot 2\lambda_{KK}A_8/8\left(\frac{a}{2}\right)^8,$$

and is, of course, independent of γ.

We can now write

$$\begin{aligned} V^{(n)} &= V^{(n)}_{ClCl} + V^{(n)}_{ClK} + V^{(n)}_{KK} + \text{constant} \\ &= \mathfrak{V}^{(n)}_{ClCl} + V^{(n)}_{ClK} + V^{(n)}_{KK} + \text{constant} \\ &= \mathfrak{V}^{(n)} + \text{constant, say,} \end{aligned}$$

where the constant refers to the internal energy of the complex group.

* Lennard-Jones & Dent, Proc. Roy. Soc. A, vol. cxii. p. 230 (1926).

† Lennard-Jones & Ingham, Proc. Roy. Soc. A, vol. cvii p. 636 (1925).

The values of $\mathfrak{V}^{(n)}$ are given in the following table, where r is measured in ångströms.

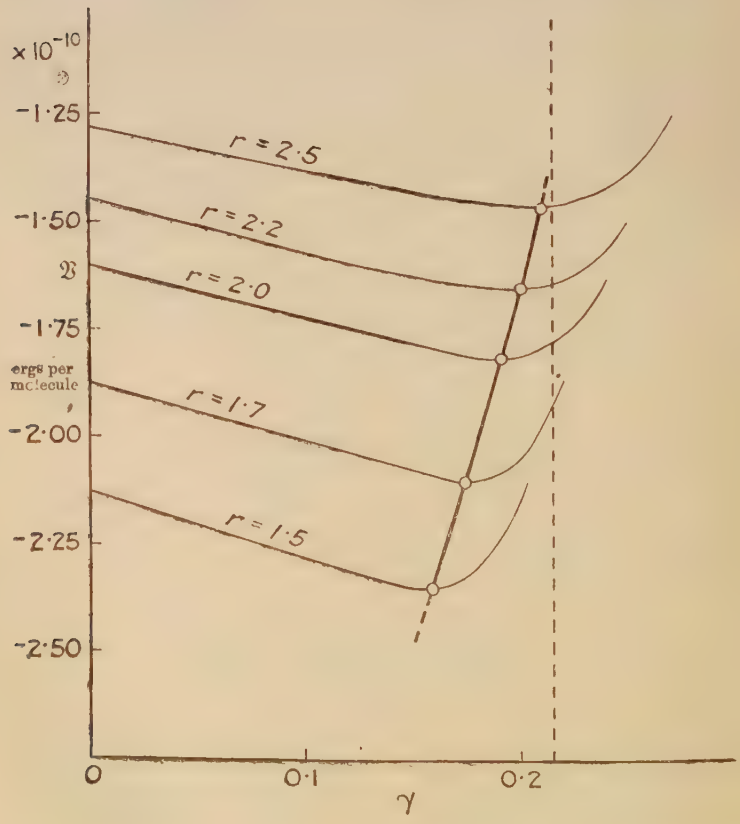
TABLE III.

Values of $\mathfrak{V}^{(n)}$ for the Crystals of K_2SnCl_6 and K_2PtCl_6.

γ	0·10	0·16̇	0·20	0·25	0·3̇
$\mathfrak{V}^{(n)}$ ...	$\frac{1\cdot557}{r^8}.10^{-12}$	$\frac{1\cdot402}{r^8}.10^{-10}$	$\frac{0\cdot764}{r^8}.10^{-9}$	$\frac{0\cdot806}{r^8}.10^{-8}$	$\frac{1\cdot112}{r^8}.10^{-6}$.

Fig. 6.

The potential energy of crystals of K_2SnCl_6 or K_2PtCl_6 for various configurations. ($= \mathfrak{V}+$constant.) The minimum of each curve gives a possible theoretical value of the crystal parameter. (The dotted line gives the corresponding result neglecting the intrinsic repulsive forces.)

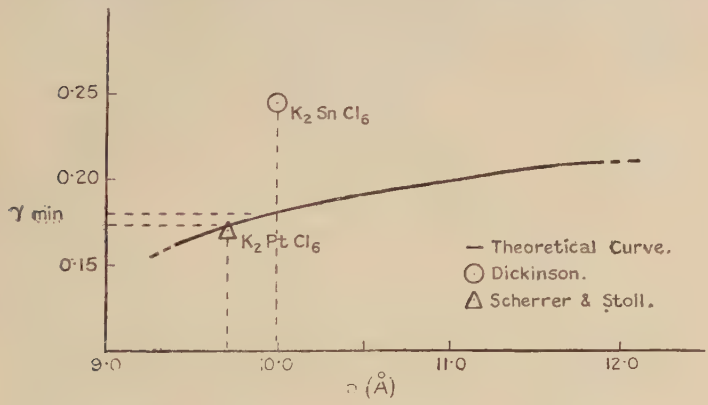


3.5.—*Determination of the Position of Stable Equilibrium.*—The total potential energy $V = V^{(e)} + V^{(n)} = V^{(e)} + \mathfrak{V}^{(n)} + \text{constant}$, $= \mathfrak{V} + \text{constant}$, say. We are now in a position to express $\mathfrak{V}$ as a function of r, for a series of values of the parameter γ. We then assign a certain numerical value to r and plot $\mathfrak{V}$ against γ. A set of such curves is shown in fig. 6.

The different values of γ corresponding to minimum values of the potential energy can then be read off from the curves. Since $r = \gamma a$, we obtain in this way a relation between γ and the length of the side of the unit cube. This is shown in fig. 7.

Fig. 7.

Theoretical relation between the crystal parameter of K_2SnCl_6 (or K_2PtCl_6) and the side of the unit cell. (Observed values: Dickinson, J. A. C. S. vol. xliv. p. 276, 1922; and Scherrer & Stoll, *Zeits. Anorg. Chem.* vol. cxxi. p. 319, 1922.)



3.6. *Discussion.*—The length of the side of the unit cube of K_2SnCl_6 is given by Dickinson as 9·91 Å., and that of K_2PtCl_6 by Scherrer and Stoll as 9·7 Å. We therefore see from the figure that the corresponding theoretical values of γ are 0·18 and 0·17 respectively, to be compared with the values 0·245 and 0·17 found experimentally.

§ 4. *The Crystal of Solid Carbon Dioxide.*

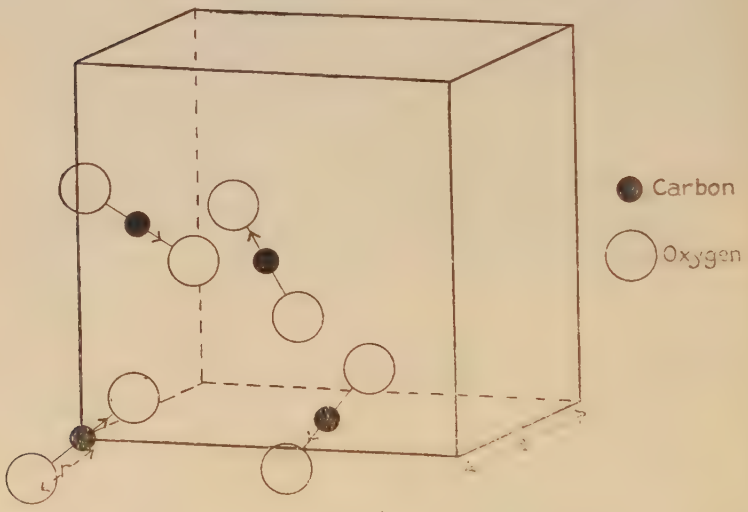
4.1. *Structure.*—As we stated in the introduction, the structure of solid carbon dioxide has been investigated by de Smedt and Keesom, and by Mark and Pohland, and the two results agree as regards the type of lattice and the edge

of the elementary cell. The carbon atoms form a face-centred cube, and the molecules of CO_2 are parallel to the diagonals of the cube, as is shown in fig. 8.

Fig. 8.

Unit cell of solid carbon dioxide containing four molecules.

(The arrows point away from the observer.)



The length of the side of the unit cube, a in the figure, is 5·63 Å.

The position of the O atoms is determined by the parameter γ, such that the smallest coordinate difference between C and O atoms is $\gamma . a$. Hence, if r is the distance between C and O atoms, $r = \sqrt{3}\gamma a$.

4.2. *Method.*—For reasons discussed in the introduction, we assume that the atoms are ionized, so that the C atoms carry fourfold positive charges and the O atoms double negative charges. Just as in the two previous cases, we consider displacements which keep the distance r constant, and finally obtain a curve connecting r and a for minimum values of the potential energy.

In this case also we have to calculate $V^{(e)}$ as well as $V^{(n)}$. Now $V^{(n)} = V^{(n)}_{OO} + V^{(n)}_{CO} + V^{(n)}_{CC}$. The calculation of $V^{(n)}_{OO}$ is easily effected, seeing that the forces between O^{--} ions are known. Compared with these forces, those between C^{++++}

ions are minute, as has been shown elsewhere *. The contribution of $V_{CC}^{(n)}$ is therefore negligible †.

As regards $V_{CO}^{(n)}$, the most important part is that which arises from the forces between the ions of the same CO_2 group. Since we keep the size of this group constant in any one set of calculations, we may regard $V_{CO}^{(n)}$ as constant. Hence we may write

$$V^{(n)} = V_{OO}^{(n)} + \text{constant},$$

and proceed to calculate $V^{(e)}$ and $V_{OO}^{(n)}$.

4.3. *Calculation of the Electrostatic Potential Energy.*—We use again the method due to Emersleben, described in section (3.3) of the preceding paragraph, and thus calculate the potential energy for the values $\gamma = 1/12$, $2/12$, and $3/12$. When γ tends to 0, with a fixed r, a tends to infinity, and therefore the electrostatic potential energy of the crystal tends to that of one molecule. We write $V^{(e)}$, the electrostatic potential energy of the crystal in ergs per molecule, $= f_1(\gamma)/r \cdot 10^{-18}$. Values of $f_1(\gamma)$ are given in the following table, and are also plotted in fig. 9.

TABLE IV.

Values of $f_1(\gamma)$ for solid CO_2.

γ	0	1/12	2/12	3/12
$f_1(\gamma)$	−3·191	−3·201	−3·491	−4·594

A check on the work is possible in the case when $\gamma = \frac{1}{4}$, for then the whole lattice is like a CaF_2 lattice with all the charges doubled (see fig. 8). The electrostatic potential energy is therefore equal to four times that of a CaF_2 crystal, or

$$4\left(-\frac{e^2}{2\gamma a} \cdot 5{\cdot}81828\right)^{\ddagger} = -\frac{4{\cdot}594}{r} \cdot 10^{-18}.$$

Values of $f_1(\gamma)$ corresponding to intermediate values of γ were found by means of an interpolation formula.

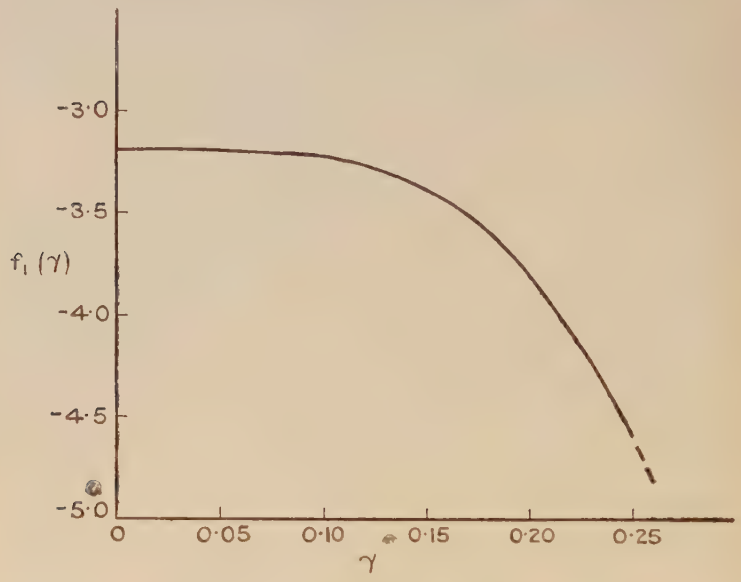
* Lennard-Jones & Dent, Proc. Roy. Soc. A, vol. cxiii. (footnote on p. 678, 1927).

† It is possible to make an estimate of $V_{CC}^{(n)}$ by using the value of the force constant ($\mu_{33} = (\frac{1}{2})^{10} \cdot (0{\cdot}0625)$) given by Topping and Chapman (Proc. Roy. Soc. A, vol. cxiii. p. 658 (1927). We find that $V_{CC}^{(n)}$ is of the order of 0·0001 per cent. of $V_{OO}^{(n)}$.

‡ Emersleben, *loc. cit.*

Fig. 9.

Curve of $f_1(\gamma)$. The electrostatic potential energy of solid carbon dioxide $= V^{(e)} = f_1(\gamma)/r \cdot 10^{-18}$ ergs per molecule.



4.4. *Calculation of* $V_{OO}^{(n)}$.—The repulsive force between two O ions at a distance r apart is given by $\lambda_{OO} r^{-n}$, where λ_{OO} is $= 17{\cdot}6$, and $n = 11$ *. This gives the force in dynes when the distance is measured in ångströms. Hence $V_{OO}^{(n)}$, the potential energy in ergs per molecule of the crystal due to the repulsive forces between O ions, is equal to

$$\tfrac{1}{2}(\lambda_{OO}/10) \Sigma \left(\frac{1}{\gamma^{10}}\right) + \text{constant} = \mathfrak{V}_{OO}^{(n)} + \text{constant, say,}$$

where the summation extends over all distances between the two O ions of one molecule and the O ions of the neighbouring molecules, and the constant represents the interaction of the two O's of one molecule.

As a first approximation we consider the effect on one CO_2 molecule of the 24 nearest oxygen ions—that is, we consider 48 distances, 4 of which are different. The values of $\mathfrak{V}_{OO}^{(n)}$ are given in the following table, where r is measured in ångstroms.

* *Loc. cit.*

TABLE V.

Values of $\mathfrak{B}_{OO}^{(n)}$ for solid CO_2.

γ	0	0·05	0·10	0·12
$\mathfrak{B}_{OO}^{(n)}$	0	$\frac{4\cdot65}{r^{10}} \cdot 10^{-16}$	$\frac{9\cdot09}{r^{10}} \cdot 10^{-13}$	$\frac{7\cdot13}{r^{10}} \cdot 10^{-12}$

γ	0·15	0·20	0·25
$\mathfrak{B}_{OO}^{(n)}$	$\frac{9\cdot12}{r^{10}} \cdot 10^{-11}$	$\frac{2\cdot42}{r^{10}} \cdot 10^{-9}$	$\frac{2\cdot59}{r^{10}} \cdot 10^{-8}$

As mentioned above, when $\gamma = \frac{1}{4}$, the whole lattice is like a CaF_2 lattice, so that the oxygens form a simple cubic system. The accurate calculation can then be made for the infinite array of O ions, by using the crystal potential constant *. This forms an effective check on the work and shows the order of accuracy. The approximate result when $\gamma = \frac{1}{4}$ is $(\frac{1}{2}\lambda_{OO}/10a^{10})\ 1\cdot27 \cdot 10^4$, while the correct result is $(\frac{1}{2}\lambda_{OO}/10a^{10})\ 1\cdot32 \cdot 10^4$, a difference of 4 per cent. This has a negligible effect on the determination of the crystal parameter.

4.5. *Determination of the Position of Stable Equilibrium.*— The total potential energy of the crystal, V, in ergs per molecule is therefore given by the following equations:

$$\begin{aligned} V = V^{(e)} + V^{(n)} &= V^{(e)} + V_{OO}^{(n)} + \text{constant}, \\ &= V^{(e)} + \mathfrak{B}_{OO}^{(n)} + \text{constant}, \\ &= \mathfrak{B} + \text{constant, say.} \end{aligned}$$

A series of numerical values is now assigned to r, and $\mathfrak{B}$ is calculated and plotted against γ. A set of such curves is shown in fig. 10, one curve (that for $r = 1\cdot00$ Å) being drawn on a larger scale in fig. 11.

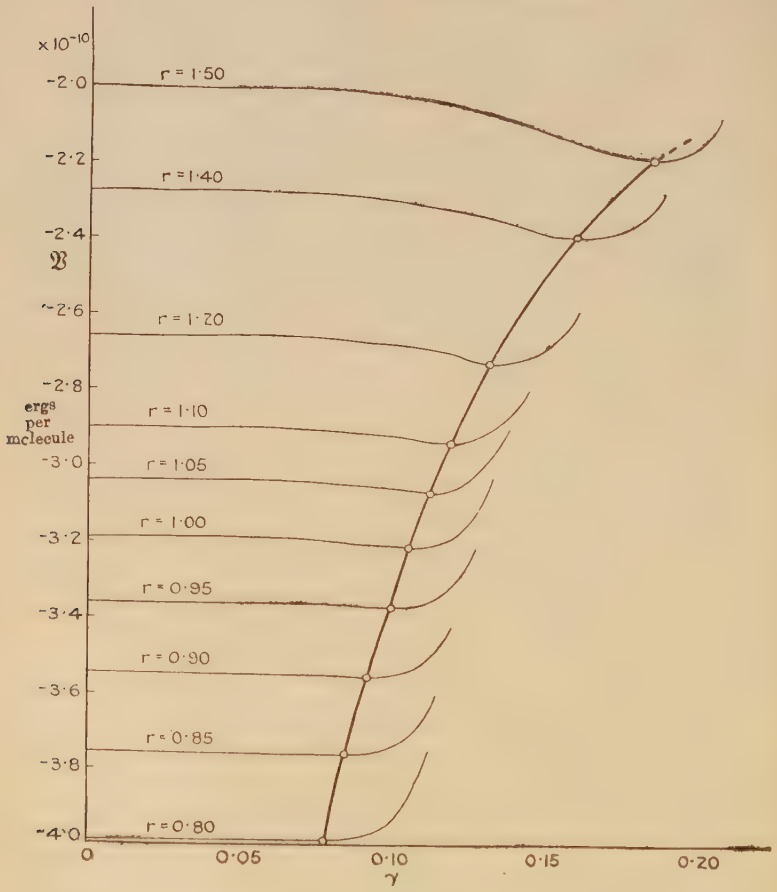
The values of γ corresponding to minimum values of the potential energy can be read off from the curves; and since $r = \sqrt{3} \cdot \gamma a$, we obtain a relation between $\gamma_{min.}$ and a. This relation is exhibited in fig. 12.

* Lennard-Jones & Ingham, *loc. cit.*

4.6. *Discussion.*—We see from the above curve that the value of r, which corresponds to the value 5·63 Å. for a

Fig. 10.

The potential energy of the crystal of solid carbon dioxide for various configurations (= $\mathfrak{V}$ + constant). The minimum of each curve gives a possible theoretical value of the crystal parameter.



found experimentally, is 0·90 A., but since the graphical method used admits of a certain inaccuracy, we prefer to give the result as 0·90 ± 0·04 Å.

Fig. 11.—One of the curves of fig. 10 drawn on a larger scale.

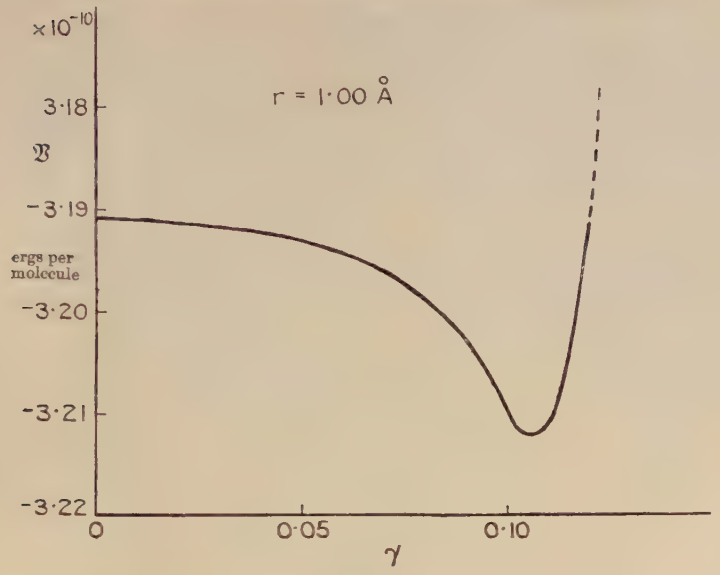
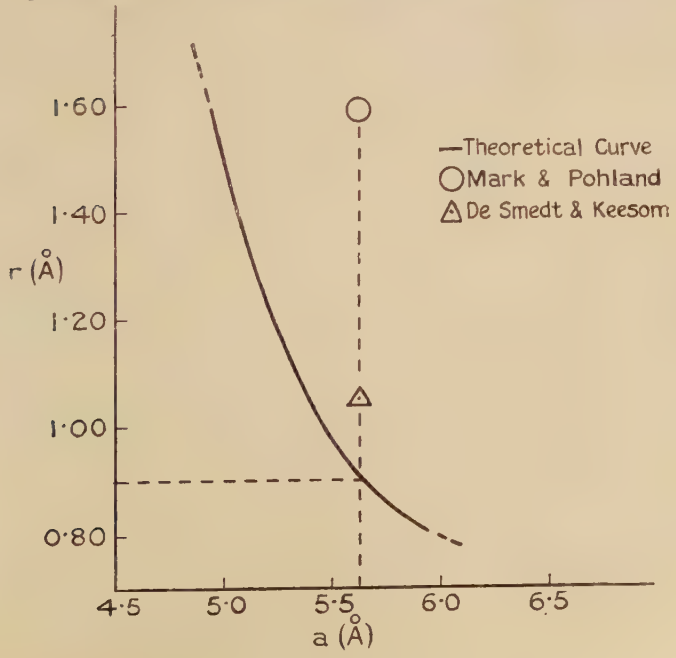


Fig. 12.

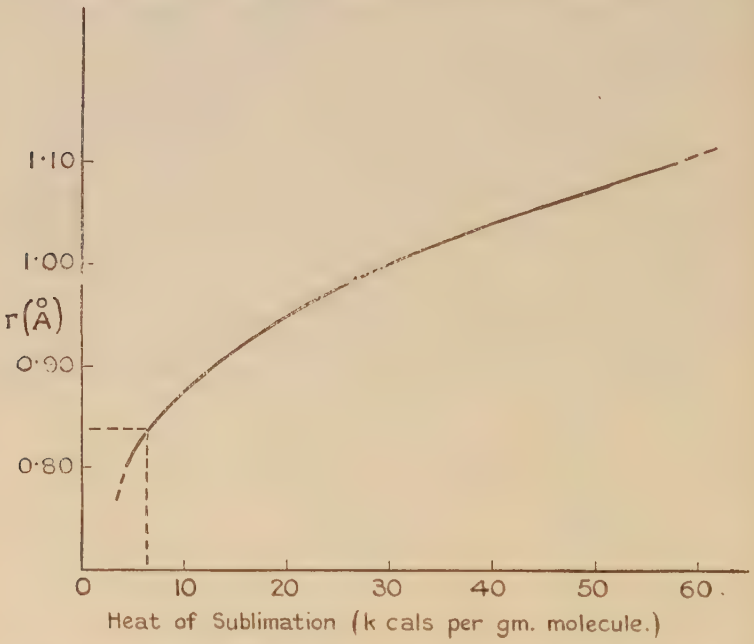
The theoretical relation between the crystal parameter and the side of the unit cell. (Observed values: Mark & Pohland, *Zeit. f. Krist.* vol. lxi. p. 293 (1925); de Smedt & Keesom, Proc. Acad. Sci. Amsterdam, vol. xxvii. p. 839 (1924), and *Zeit. f. Krist.* vol. lxii. p. 312 (1925).



An interesting check on this result is possible by using the curves given in fig. 10 to give a theoretical estimate of the heat of sublimation. The difference in the minimum value of $\mathfrak{B}$ and the value for $\gamma=0$ is the work required to separate the molecules in the crystal to an infinite distance

Fig. 13.

Theoretical relation between the heat of sublimation of solid CO_2 and the distance between a C and an O ion in the CO_2 molecule.



from one another *. If we neglect any change in shape or size of the molecule on sublimation, we can compare these theoretical values directly with the heat of sublimation found experimentally. The theoretical relation between the heat of sublimation and r is shown in fig. 13.

The heat of vaporization of CO_2 at absolute zero is given by Eucken, Karwat, and Fried † as 6313 calories. The corresponding value of r from fig. 13 is 0·84 A. It is to

* The fact that we have omitted the potential energy due to the repulsive forces of the ions of the same CO_2 molecule will not affect this *difference*.

† Eucken, Karwat, & Fried, *Zeit. f. Phys.* vol. xxix. p. 29 (1924).

be observed that any change in the shape or size of the CO_2 molecule will decrease the heat of sublimation found theoretically and therefore shift the curve in fig. 13 further to the left. This shift would cause an increase in the value 0·84 Å. for r, so that we have to compare the two values $0{\cdot}09 \pm 0{\cdot}04$ Å. and (0·84+) Å.

We have so far supposed that the electrostatic and the repulsive force centres of an O^{--} ion coincide. If, however, the distortion of the O ion in the presence of the C ion be considered, it is clear that the repulsive force centre (O_r) and the electrostatic force centre (O_e) are each displaced from the nucleus (O) in such a way that $CO_e < CO_r < CO$. An estimate of the effect of such distortion can be found by putting $CO_r = k \,.\, CO_e$, when $k > 1$ and by giving k a numerical value. For instance, if $k = 1{\cdot}1$, which represents considerable distortion, we find that the effect is to move the curve in fig. 12 to the left, thus giving a value of r corresponding to a observed equal to about 0·55 Å., and a value of the distance CO equal to 0·62 Å. The effect of distortion is thus seen to decrease the distance between the two nuclei. The theoretical value $0{\cdot}90 \pm 0{\cdot}04$ Å. given above is therefore an upper limit. This result seems to negative the value 1·59 Å. given by Mark and Pohland.

As mentioned in the introduction, the theoretical value here given is of the same magnitude as the values for the distance between C and O ions in a gaseous CO_2 molecule given by Schaefer and Philipps (1·02 Å.) and by Dennison (0·96 Å.).

Another comparison is possible. The present authors have made a determination of the size of the CO_3 group in carbonate crystals *, and find that the distance C to O is 1·08 Å., and the distance O to O 1·87 Å., whereas the corresponding distances for CO_2 are about 0·90 Å. and 1·80 Å. A consideration of the formation of the CO_2 molecule from a $(CO_3)^{--}$ group and of the redistribution of forces shows that a shrinking in the distance between oxygens is to be expected. We see that the calculations do, in fact, give a decrease in this distance of 0·07 Å., and hence the results obtained for the CO_2 molecule and the CO_3^{--} group are consistent.

* Lennard-Jones & Dent, *loc. cit.*

CXVII. *Notices respecting New Books.*

Experimental Optics. By G. F. C. Searle. (Cambridge University Press. 16*s.*)

A SATISFACTORY treatment of geometrical optics, suitable for the student of physics, has hitherto been sadly to seek in English scientific literature. The standard text-books on light treat the subject in a very perfunctory way, and the books specially devoted to this branch of knowledge are either in the nature of geometrical treatises, entirely divorced from the laboratory, or else addressed to the instrument maker. It is, therefore, no exaggeration to say that Dr. Searle's book, in which he embodies the results of his long experience as the inspiring leader of the instructional courses in the Cavendish Laboratory, fulfils a need which has been very seriously felt by many university teachers.

The book contains a description of seventy laboratory experiments, covering the whole field of geometrical optics, and, in addition, treats of problems in which geometrical optics and physical optics are both involved, such as the measurement of the thicknesses of films by interference methods, the measurement of resolving power, and the manipulation of the diffraction grating and zone plate. The plan adopted is to give a theoretical discussion of the problem to be handled and the principles involved, then a description of the apparatus and experimental method, with all necessary cautions and hints, and finally, when it seems helpful, an example of a calculation made with the actual figures obtained in the Cavendish Laboratory. Particular attention is devoted to the correct way of adjusting and controlling apparatus, such as the spectrometer, whose readings for immediate service the student generally tends to take for granted.

Most physicists know of Dr. Searle's ingenuity in contriving apparatus of simple design and geometrical construction which shall allow accurate measurements to be made, and the use of many of his own devices which can now be purchased, such as the Searle goniometer and the revolving table for measuring curvatures, is described in the book. There is a variety of interesting matter which is off the beaten track, such as the use of the pentagonal prism (which could be purchased for a few pence when war stores were being freely sold) to carry out a laboratory version of the naval range finder, the very full experimental treatment of astigmatism and focal lines, and the determination of the thickness of a film by a "banded" spectrum. On the theoretical side mention may be made of the calculation of the curvature of the image of the slit in the prism spectrometer, which is omitted in many books.

Protest must be made against the sign convention adopted by Dr. Searle in his treatment of lenses, which makes the value of v positive when the image is real, and the radius of curvature

positive when the surface is convex to the air, on either side of the lens. It seems much better to adopt the ordinary Cartesian convention, which is, in fact, receiving general acceptance. It is also a pity that Dr. Searle has not adopted the convention of an index, especially in view of the lack of page numbers in the list of contents.

Every page of Dr. Searle's book bears witness to precision of thought and long laboratory experience coupled with an enthusiastic ingenuity. It should do much to improve the teaching of experimental optics in our university laboratories, where it has for so long suffered comparative neglect.

International Critical Tables of Numerical Data, Physics, Chemistry, and Technology. (McGraw-Hill Book Company. $12.00.)

At the organizing meeting of the International Union of Pure and Applied Chemistry held in London in 1919, it was decided that a collection of Critical Tables of physical and chemical constants should be undertaken, and the financing and editing of the undertaking were assigned to the United States of America. The National Research Council of the United States made itself responsible for the project and created a Board of Trustees and a Board of Editors, at the head of which was and is Dr. E. W. Washburn. The actual work of compilation was started in 1922, and the volume before us, which appeared in 1926, is the first instalment of a work which is to be completed in six such volumes. The labour of an undertaking on this scale is prodigious, and has necessitated an elaborate organization of Corresponding Editors and Cooperating Experts in, apparently, every country of scientific significance—with the trifling exception of Germany.

Apart from the various prefaces, introductions, and other preliminary matter (including a table of national and local weights and measures which occupies twelve pages, and tells at some length of the systems of weights prevailing in Anam—thus spelt in the Tables—and the Balearic Islands, but does not mention such things as the Leipsig ell cited by von Guericke), the present volume is divided into five sections, viz., Laboratory Technique, Physical Properties of Chemical Substances, Radioactivity, Astronomical and Geodetic Data, and Aerodynamics. The first section includes such things as Thermometry, by various hands, which contains a useful section on laboratory method for maintaining constant temperatures, both high and low; Psychometry; and High Vacuum Technique, the last-named division consisting of a collection of miscellaneous formulæ bearing on the behaviour of gases at very low pressures. The Physical Properties of Chemical Substance Table gives the melting-point, density, boiling-point, refractive index, and occasionally other properties of a vast range of chemical substances, and, further, contains a "Property-Substance" Table, which gives under tabulated values of the boiling-point, melting-point, and density

the names of substances having that particular value. The arrangement in the main tables is based upon a new system of key numbers which must be mastered before a given substance can be found; it is not very difficult. These chemical tables occupy the main part of the volume—some 260 pages out of 412—and are very complete. The twenty pages of radioactive data which comprise the third section contain matter which is by this division separated from other ionic and electronic information. The section on Astronomical Data, which is eleven pages, naturally shows a very high degree of selection. The volume concludes with some miscellaneous curves of aerodynamic interest.

The range of the volume is very wide. Not only do we have aerodynamics and selected physical properties of stars and nebulæ, but the chemical section includes tables of sweetening agents and odoriferous materials, classed as such, and three pages of curves pertaining to "Dispersoidology." There is nothing like this in Landolt-Börnstein. The book bears marked traces of masses of good advice and editorial complacency.

It should be noted that these tables are critical, that is, the value of a given constant which is, in the opinion of the editor or his agent, the most reliable, will be given, and not the various, possibly very different, values obtained by different experimenters. No doubt every large library will have to possess a copy of these tables, the real use of which the next year or two will establish.

Colloid Chemistry. By Selected International Contributors. Collected and edited by JEROME ALEXANDER. (The Chemical Catalog Company. Price $15.)

THIS is a collected work, consisting of sixty chapters by different authors (a few of whom are represented twice), which covers the whole range of colloid chemistry as studied in the laboratory. It is apparently intended to issue two further volumes, one dealing with colloid chemistry from the point of view of biology and medicine, and the other with colloid chemistry in technology. The chapters are very unequal in length, varying from seventy-five pages to less than a page and a half, and the reasons for including some of the shorter ones are a little obscure. The term "colloid chemistry" has been interpreted in the widest sense—for instance, there are two very interesting pages of notes by Professor H. N. Russell on Dispersed Systems in Astronomy, dealing with such things as comets' tails and Saturn's rings, two more by Professor W. D. MacMillan on The Planetesimal Hypothesis, and an excellent description of the determination of e by Professor Millikan. Among the larger chapters, on matters more usually encountered in books on colloid chemistry, may be mentioned The Theory of the Colloid State of Matter, by Professor P. P. von Weimarn; Surface Energy and Surface Tension, by Professor W. D. Harkins; and Sedimentation Analysis and its Applications to Clays and Precipitates, by Professor Sven Odén.

Nearly every name of eminence in the field of colloid chemistry occurs in the list of authors: in addition to those just cited we have Sir W. B. Hardy, E. F. Burton, Einstein, Freundlich, Zsigmondy, Svedberg, Hatschek, and others who are here omitted in no invidious spirit, but for reasons of space. The physical aspects of the subject, such as surface tension and viscosity problems, are well represented, and readers of the Philosophical Magazine can rely upon finding excellent summaries, with bibliographies, of many regions of research in which there is plenty of room for precise investigation.

The preface is notable for a rare collection of pretentious platitudes and quotations of doubtful appropriateness.

The Age of the Earth: An Introduction to Geological Ideas. By Prof. Arthur Holmes. (Benn, 1927. Pp. 80. 6*d.*)

Prof. Holmes's semi-popular book of 1913, with a similar title to that of the present pamphlet, is now one of the classics of the subject. In the work under review he gives a very full and up-to-date account of the issues involved; nothing of importance seems to have escaped mention. In addition, the history of the development of ideas in general geology, as well as in the special department chiefly under consideration, is clearly outlined. Nor has moral uplift been neglected. The only criticism the reviewer can make is that the theory of magmatic cycles is described in such a way as to suggest that it is a well-established theory and not an exceedingly questionable hypothesis. But this affects only about two pages of an excellent work. H. J.

The Spectroscopy of X-Rays. By Manne Siegbahn. Translated by G. A. Lindsay. (Oxford University Press.)

In no branch of Physics have greater strides been made than in the investigation of X-Rays. Prof. Siegbahn has been well known as one of the foremost experimentalists in this branch of Science, and the outcome of some of his researches and that of his co-workers is set out in this fine volume.

Striking examples of the increasing accuracy attained during the last ten years are given in the Preface—a comparison of the values of the wave-length of Cu–K–α_1 line from Moseley's 1913 value to Prof. Siegbahn's results published by him two years ago, and again in considering the invalidity of the Bragg interference equation with the small correction required for spectra of the first order in particular.

Other chapters naturally touch on the related subject of atomic structure and the study of atomic models. A concise account of the essential details of the theories, due to Bohr and Sommerfeld, is given in a later chapter on the Systematic Arrangment and Theory of X-Ray Spectra. Numerous experimental results are also tabulated in connexion with Emission and Absorption

Spectra. A Bibliography extending over twenty pages gives references to the original papers dealing with X-rays published up to 1924.

The Appendix of Tables contains a mass of information relating to reflexion angles and the principal X-ray lines of the elements, in order of their wave-lengths.

Still further progress has been made since the the appearance of this volume, and in due time a second edition of this comprehensive work will be forthcoming with addition and revisions consequent upon Prof. Siegbahn's most recent and accurate experimental results.

Historic Instruments for the Advancement of Science. By R. T. Gunther. (Oxford University Press. 2*s.* 6*d.* net.)

A Handbook to the Oxford Collection of Scientific Instruments exhibited in the Old Ashmolean Buildings. "For the Advancement of Science" is appropriately added to the title of this guide: "the knowledge of Nature is very necessary to humaine life, and that knowledge cannot be soe well and usefully attain'd except the history of Nature be knowne and considered." The exhibits are of great interest in the study of Astronomy, Physics, and allied subjects. The fine collection of astrolabes includes three Persian examples, with dedications by the makers to the ruling Sultan. "May his justice and his benefits spread over the worlds, while the spheres revolve and the planets continue their courses." Orreries, several varieties of dials, globes, and calculators are also represented.

The Handbook closes with some interesting information relating to early reflecting and refracting telescopes and the Hooke and Marshall microscopes.

The Enlarged Heat Drop Tables. Calculated by Hubert Moss, D.Sc. (London: Edward Arnold & Co. 10*s.* 6*d.* net.)

This set of tables is supplementary to those published some few years ago for the British Electrical and Allied Manufacturers' Association, the initial pressure-gauges, in lb. per square inch, extending as far as 400 lb. Dr. Moss has calculated tables for pressure from 400 lb. to 2000 lb. per inch gauge, and added further values for the range 50 to 400, with final pressures of mercury vacua from 29·2 to 29·5 inches. The intervals are sufficiently close in both cases to give intermediate values by simple interpolation. An example of the correction required beyond first difference interpolation is given in the Preface.

As indicated by the Author, the tables are based on Prof. H. L. Callendar's equations ('Enlarged Callendar Steam Tables': Edward Arnold & Co., 1924).

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

Fig. 4.

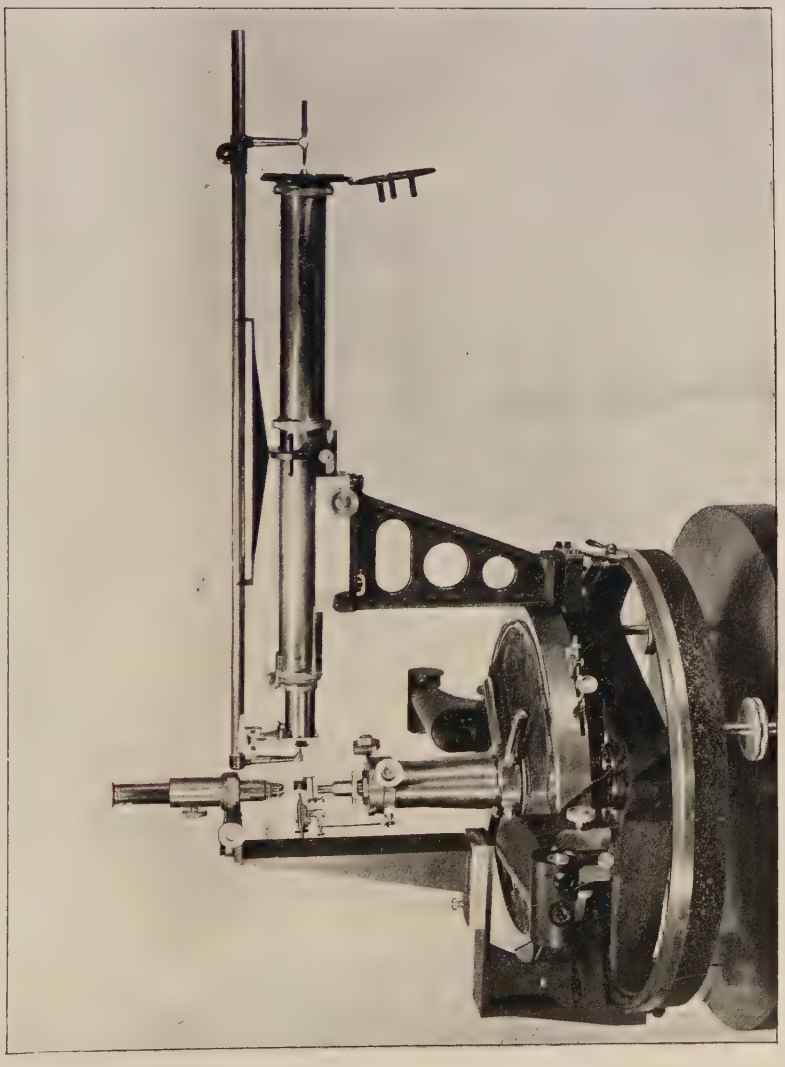
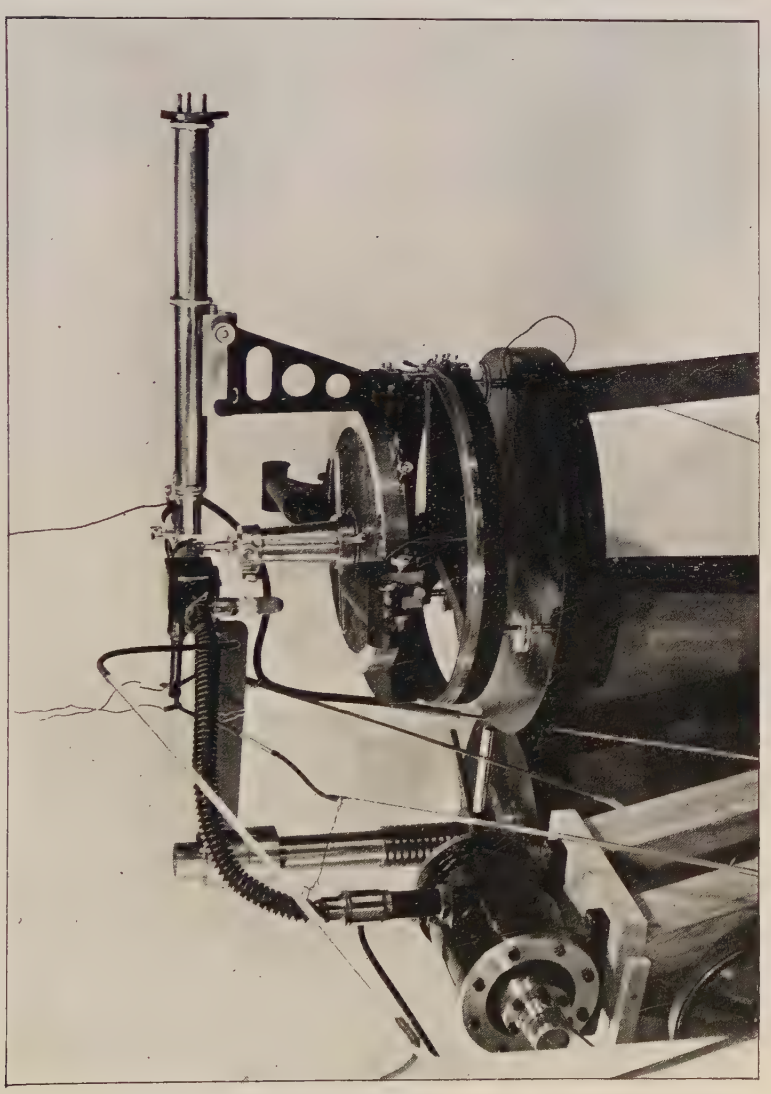


Fig. 5.



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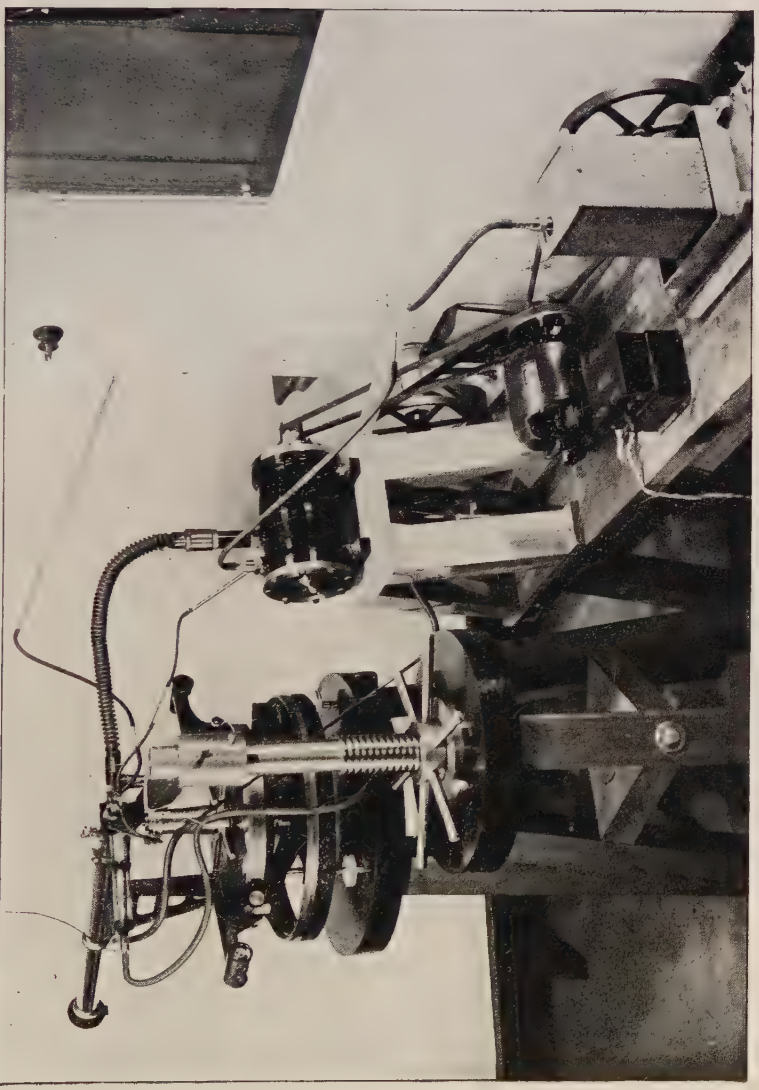

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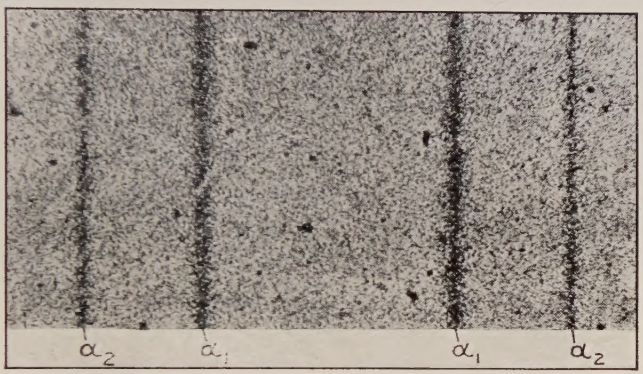

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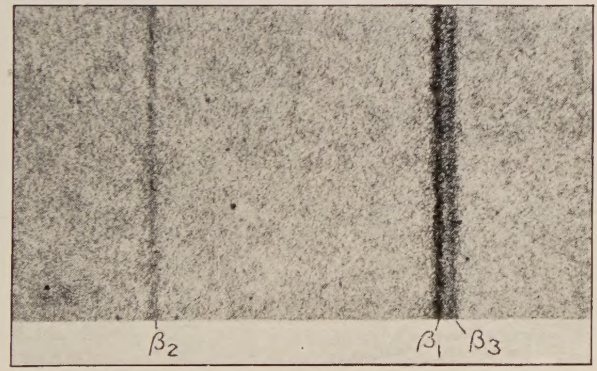
Fig. 8.



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(*a*)
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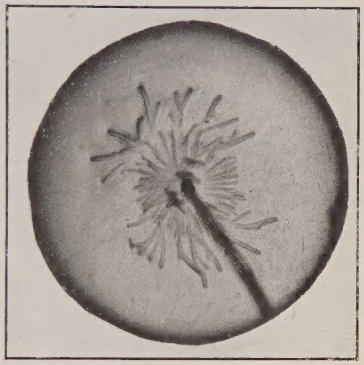

(*b*)
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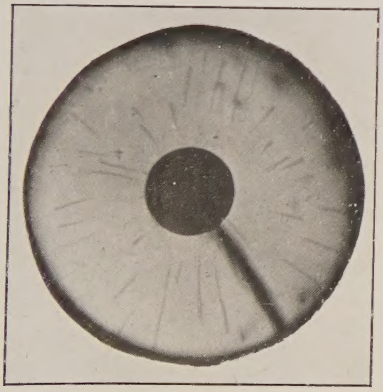

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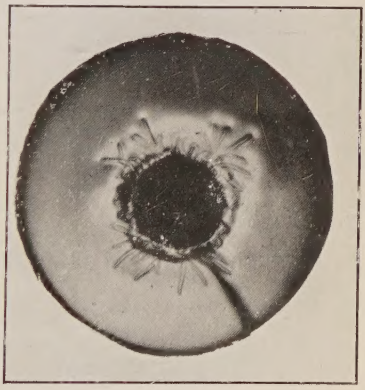

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Spherical Electrode –